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AFML-TR-69-191

**ELECTROLYTIC GROWTH AND PROPERTIES OF
TRANSITION METAL COMPOUND SINGLE CRYSTALS**

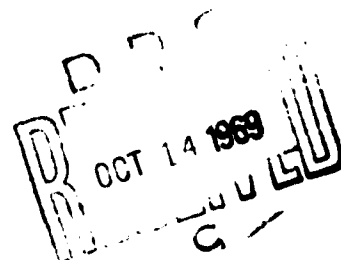
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TECHNICAL REPORT AFML-TR-69-191

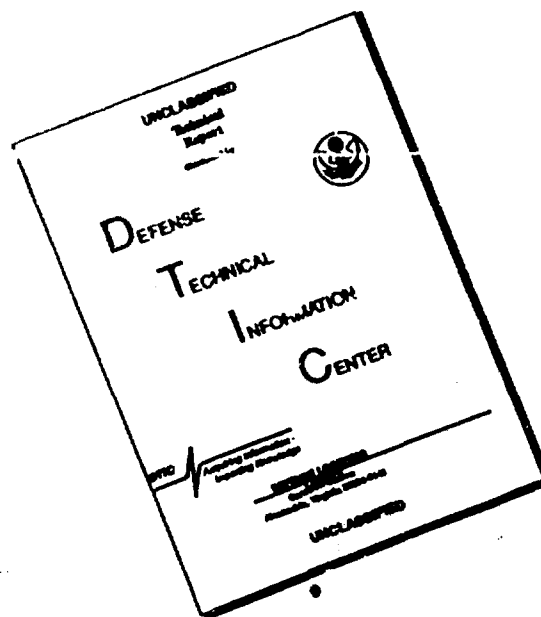
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BROWN UNIVERSITY**

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FOREWORD

This report was prepared by Brown University, Providence, Rhode Island, under USAF Contract AF 33(615)-3844. The contract was initiated under Project No. 7367, "Research on Characterization and Properties of Materials" and continued under Project No. 7371, "Exploratory Development in Electrical, Electronic, and Magnetic Materials". The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. Dr. Emile Rutner was the Project Scientist.

This technical report has been reviewed and approved.

Hyman Marcus

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ABSTRACT

Single crystals of FeP, Fe₂P, CoAs₂ and FeAs₂ were grown by either electrolysis of fused salts or chemical transport. Of these four compounds prepared to date, extensive studies have been carried out on well-characterized crystals of FeP. This compound exhibits metallic behavior throughout the temperature range of 4.2°K to 298°K. Anomalies in the magnetic susceptibility and resistivity curves at about 120°K have been correlated with an ordered antiferromagnetic spiral. The other compounds have been chemically analyzed and their electrical and magnetic properties are being characterized.

In addition, crystals of cadmium sulfide have been grown from the vapor phase with dimensions 12 mm long x 9 mm wide x 0.2 mm thick. The resistivity of these crystals was found to be 2×10^6 ohm-cm at room temperature. On heating these crystals to 800°C for 4 hours and quenching to room temperature, the resistivity was found to be 219.3 ohm-cm. Samples of these crystals will be delivered to Dr. P. Hemenger at Wright-Patterson.

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SECTION I
INTRODUCTION

The principle purpose of this project has remained the development of new techniques for the preparation of new refractory metal compounds in the form of single crystals. Many of the materials being studied today are polycrystalline and are prepared by standard ceramic techniques. The relatively few single crystals produced are obtained from the melt or are flux grown. Very little work has been reported on the growth of high-melting refractory transition metal phosphides, arsenides, etc. Those that have been grown usually are of uncertain composition. In addition to the preparation of transition metal phosphides and arsenides by electrolysis and chemical transport, we have been developing a method for the growth of metal sulfide single crystals by vapor growth. During this year our efforts have concentrated on the preparation of pure (high resistivity) cadmium sulfide as well as zinc doped single crystals. The electrical properties of these compounds can be drastically altered by appropriate heat treatment.

The results of this year's progress on transition metal phosphides are summarized in a paper which is included in this report. The work to date on the arsenides and cadmium sulfide single crystal growth is also included in this technical report.

It will be seen that the emphasis has been placed on the growth of pure well-defined single crystals and also attempts have been made to correlate the effects of purity on both the magnetic interactions and the transport properties.

SECTION II

TRANSITION METAL ARSENIDES (MAs_2)

The transition metal arsenides of the MX_2 formula can adopt any of six structure types as shown in the table below.

 MAs_2 Compounds and Structures

Ti(a)	V(b)	Cr(-)	Mn(-)	Fe(m)	Co(d)	Ni(p,m)
Zr(c)	Nb(b)	Mo(b)	Tc(-)	Ru(m)	Rh(d)	Pd(p)
Hf(c)	Ta(b)	W(b)	Re(-)	Os(m)	Ir(d)	Pt(p)
KEY a = $TiAs_2$ structure d = arsenopyrite b = $NbAs_2$ structure m = marcasite c = $PbCl_2$ structure p = pyrite - not formed						

There are general structural similarities among the compounds on both the left and right sides of the table. The compounds on the left have the cations in a trigonal prismatic coordination; whereas the compounds on the right have the cations in a nearly octahedral coordination. The compounds that will be initially studied are those having nearly octahedral coordination, namely, $FeAs_2$, $CoAs_2$ and $NiAs_2$. As can be seen from the above table, these arsenides occur in the following structure types: pyrite, marcasite, and arsenopyrite. All three are similar in that the anions form pairs and are coordinated to three other metal atoms to form a distorted tetrahedron. The pyrite structure can be derived from the rocksalt structure by placing two anions on each anion

site and by pulling them apart along a body diagonal. The overall symmetry of pyrite is cubic just as the overall symmetry for rocksalt is cubic. The marcasite structure can be derived from the hexagonal closest packed CdI_2 structure which has completely filled and empty cation layers alternating between the closest packed anion layers. To form the marcasite structure $1/2$ of the cations in the filled layer are translated to the empty layer. A final step of rotating the octahedra in such a way that anion-anion pairs are formed results in the marcasite structure. The arsenopyrite structure is related to the marcasite by a distortion in such a way that the cations form both short and long interatomic distances. This results in the formation of cation pairs in the direction of the short cation interatomic distances.

The work being performed in this laboratory has been limited to the first row transition metal compounds FeAs_2 and CoAs_2 . In the next four sections a review of the previous work on these compounds is presented and a summary of the new work in this laboratory is described.

PREVIOUS INVESTIGATIONS OF FeAs_2 .

Holmes claimed to have synthesized FeAs_2 and to have studied it by X-ray techniques⁽¹⁾. He reports that previous studies cannot be validated because X-ray phase analyses were never carried out, and he also explains the great variations in reported stoichiometries as due to inhomogeneity of the samples. Holmes reports the preparation of FeAs_2 by reaction of the elements in silica tubes between the temperatures of 535 and 1050 degrees.

Heyding and Calvert⁽²⁾ confirmed the appearance of FeAs_2 and reported $\text{Fe}(\text{Fe}_x\text{As}_{2-x})$ with an As/Fe ratio of 1.93. The preparation is reported to occur at "moderate temperatures," but they report that when quenched from above

700 degrees considerable quantities of arsenic separate out. Further details of the preparation are reported in one of their earlier papers on metal-rich arsenides⁽³⁾. Analyses showed that the products were within .03 weight per cent of the original mixture.

Roseboom⁽⁴⁾ prepared loellingite with a homogeneity range from $\text{FeAs}_{1.98}$ to FeAs_2 at 800 degrees. A high pressure synthesis of FeAs_2 is also reported in the literature⁽⁵⁾.

The preparation of single crystals of FeAs_2 grown by the chemical transport method has not been reported. In the light of the reported homogeneity range of FeAs_2 , it would be of interest to prepare single crystals with varying arsenic content and then to examine the electrical and magnetic properties with respect to the variation in stoichiometry.

Hulliger⁽⁶⁾ first reported synthetic FeAs_2 as being a semiconductor with a band gap of .2ev, but his measurements were not accompanied by analysis of the compounds studied. More recently the semiconducting properties of the natural mineral were reported. Several differences were readily noticed. Hulliger measured his samples from room temperature to 500 degrees and observed a continuous decrease in resistivity with an increase in temperature. Johnson et al.⁽⁷⁾ measured the resistivity from liquid nitrogen to 900 degrees and reported an increase in resistivity between liquid nitrogen and about 400 degrees. From 400 to 900 degrees the resistivity decreased. This decrease may be related to a loss of arsenic at the higher temperatures, but the authors do not report loss of arsenic. Measurements on single crystals have not been reported.

The natural mineral of FeAs_2 has been reported to have a paramagnetic moment which is temperature dependent and resembles the moment of neutral iron⁽⁸⁾. A recent review by Hulliger⁽⁹⁾ reports that FeAs_2 has a spin moment

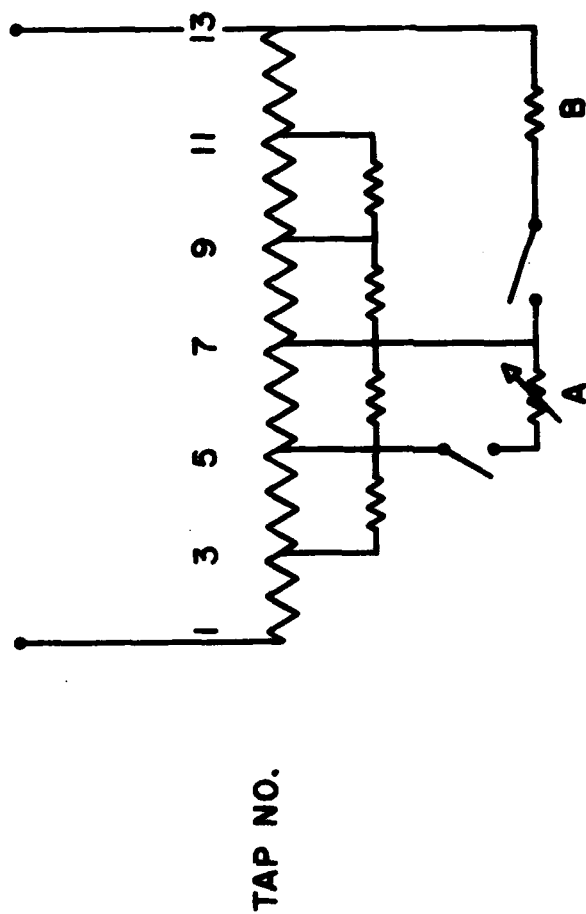
of zero and is not paramagnetic. Holseth and Kjekshus⁽¹⁰⁾ report a very weak temperature dependent paramagnetism for the compound.

An article on the Mössbauer studies of marcasite-type compounds used information from a study of the analogous natural mineral loellingite⁽¹¹⁾. The important points made were that the isomer shift of the FeS_2 pyrite and the FeAs_2 loellingite were quite similar at 300 degrees Kelvin. This is particularly interesting since the formal charge on the iron in these compounds is +2 and +4 respectively. The increased covalency of the arsenic could account for the unexpected value of the isomer shift in FeAs_2 . The large quadrupole splitting in FeAs_2 is indicative of the distortion from cubic surroundings which is inherent in the loellingite structure.

PRESENT STUDY OF FeAs_2 .

FeAs_2 single crystals have been grown in this laboratory by the chemical transport method for the first time, but numerous attempts at the preparation of the polycrystalline powder have failed. Density measurements and chemical analyses of the single crystals definitely indicate a homogeneity range which lies close to the FeAs_2 composition. Furthermore, it will be shown that chemical transport or the use of high pressure is able to achieve the preparation of FeAs_2 where direct combination of the elements under ordinary conditions has failed.

Single crystals of FeAs_2 were grown in a specially built furnace (Figure 1). The furnace consists of an alumina core which is wound with resistive heating wire with taps every 1.5 inches apart for a total of 13 taps. Alundum cement is placed around the windings for both heat conduction and for some structural support. This assembly is placed into a transite shell and packed with vermiculite insulation before the end covers are put on. The taps are



A = growth zone resistor

B = back transport resistor

Figure 1 Simplified Diagram of Transport Furnace

pulled through drilled holes in the furnace shell and are wound around individual posts so that resistors can be placed across the taps to achieve various furnace profiles. A temperature dip, which will be called the growth zone of the furnace, can be made by selectively adding resistors between taps as illustrated in the simplified diagram of the furnace. By changing the resistance, the temperature dip can be controlled. A panel outside the furnace has been designed so that the various resistors can be placed into the circuit so that the temperature gradient (dip) can be gradually introduced into the furnace over a period of time. This slow programming is necessary in order to achieve few nucleation sites and large single crystals. A special resistor is placed in the charge end of the furnace so that it can be lowered in temperature. When this resistor is in the circuit, the process is called back transport which is used to remove possible nucleation sites which are introduced when the material is added to the transport tube.

The single crystals of FeAs_2 were prepared by the chemical transport method using either iodine or chlorine as the transport agent. The charge in all cases consisted of unreacted iron and arsenic in the mole ratio of 1:1. The best transport occurred with chlorine at a pressure of 75 torr. Crystals have also been grown with 25 torr chlorine and with iodine in a concentration of 5mg/cc. A charge temperature of 800 degrees with a growth zone of 765 degrees has been used in most of the successful experiments in crystal growth. Crystals 3 - 5 mm in length have been grown by the above method. The crystals are always well-shaped with smooth faces and sharp well-defined edges.

Density and chemical analyses have been measured on different batches of transported crystals. On two different batches of crystals, the density and chemical analyses agreed within each batch but differed between batches.

This indicates a homogeneity range as illustrated in the table below.

<u>Batch</u>	<u>Fe Analysis</u>	<u>Calculated Formula</u>	<u>Density</u>	<u>Calculated Formula</u>
Theory	27.15%	FeAs_2	7.46	FeAs_2
GHR-108	25.7	$\text{FeAs}_{2.15}$	7.67	$\text{FeAs}_{2.07}$
GHR-269	25.6	$\text{FeAs}_{1.95}$	7.37	$\text{FeAs}_{1.95}$

The crystals were analyzed for the presence of halide transport agent which might be trapped in the lattice. No halide was detected in the transported crystals.

It is intended to pursue the study of the stoichiometry range of FeAs_2 as a function of the transport agent used, the concentration of the transport agent, the temperature conditions of growth, and the mole ratios of starting materials used. A study of the electrical conductivity and magnetic susceptibility of these crystals, which have a homogeneity range, will be interesting in order to observe the effect of varying arsenic content on the electrical and magnetic properties.

The preparation of the polycrystalline powder has presented unexpected difficulty. In no case was the stoichiometric FeAs_2 powder prepared. Direct combination of the elements in the mole ratios of iron to arsenic varying from 1:1.75 up to 1:3.5 failed to give the stoichiometric powders. Analysis of the resulting powder indicated a stoichiometry of $\text{FeAs}_{1.71}$ to $\text{FeAs}_{1.78}$. The X-ray patterns of the products showed FeAs_2 and arsenic, but no FeAs was noticed. Comparison of the method of direct combination of the elements with that of chemical transport indicates that the mechanism by which the chemical transport operates enables the formation of FeAs_2 whereas direct combination of the elements under normal conditions does not yield the desired products.

PREVIOUS INVESTIGATIONS OF CoAs_2 .

As recently as 1947 the existence of CoAs_2 was in doubt⁽¹⁾, but by 1963 at least three other authors^(2,4,7) claimed to prepare the polycrystalline powder. No chemical analyses have been reported by any of the last three authors. CoAs_2 belongs to the group of compounds having the closely related marcasite, loellingite, or arsenopyrite structures. A single crystal analysis⁽¹²⁾ has been carried out on CoAs_2 , but the reliability factor was a high 21% which casts some question on the accuracy of the determination. Some of the problem is caused by the high absorption of the elements, but nevertheless the reliability factor would have to be considerably reduced to qualify as a good determination.

Magnetic susceptibility measurements by Hulliger⁽¹³⁾ and by Bennett and Heyding⁽¹⁴⁾ differ. Hulliger reports a weakly paramagnetic moment throughout his temperature range from 85 to 293 degrees Kelvin. This moment corresponds to only a fraction of one unpaired electron per cobalt atom. Bennett and Heyding report that CoAs_2 is diamagnetic above 175 degrees Kelvin and has a weak paramagnetic moment below this temperature. It should be pointed out that both authors report strong diamagnetism for the isostructural compounds RhAs_2 and IrAs_2 . The bulk properties were measured on polycrystalline CoAs_2 .

Hulliger reported a band gap of .15 ev on the polycrystalline powder of semiconducting CoAs_2 . No further detail of electrical transport properties was reported.

PRESENT STUDY OF CoAs_2 .

In this laboratory CoAs_2 was prepared in both the polycrystalline form and in single crystals. Stoichiometric quantities of the reduced cobalt and arsenic, the latter having been heated under vacuum to 200 degrees to remove

oxide, were weighed into silica tubes which subsequently were evacuated and sealed. The preparation of CoAs_2 at 700 degrees seems to be ideal because there is complete reaction after two grindings and there is no silica flaking of the reaction tube at this temperature.

Single crystals of CoAs_2 were grown by the chemical transport method in a specially designed furnace which was previously described. For the single crystal preparation the charge consists of the reacted polycrystalline mass and the transport agent is chlorine with a pressure of 25 torr. After one to two days of back transport to remove excess nucleation sites, the furnace is equilibrated at 800 degrees and then the growth zone is programmed down to 765 over a period of two days. Crystal growth is continued another three or four days. The resulting crystals grow as polyhedra with shiny smooth faces and sharp edges. The crystals are a suitable size for electrical measurements, which have never been reported for single crystals of CoAs_2 .

A single crystal X-ray structural investigation has been undertaken to improve on the previous determination which obtained a 21% reliability factor. The absorption problem is being corrected by using a crystal which has been ground into a sphere. This enables one to apply isotropic corrections for absorption to get more accurate data for the solution of the structure.

REFERENCES

- (1) R. J. Holmes, Bull. Geo. Soc. Am., 58, 229 (1947).
- (2) R. D. Heyding and L. D. Calvert, Can. J. Chem., 38, 313 (1960).
- (3) R. D. Heyding and L. D. Calvert, *ibid.*, 35, 449 (1957).
- (4) E. Roseboom, Am. Mineral., 48, 271 (1963).
- (5) P. C. Donahue et al., Inorg. Chem., 7, 988 (1968).
- (6) F. Hulliger, Helv. Phys. Acta, 32, 615 (1959).
- (7) W. D. Johnson et al., J. Less-Common Metals, 8, 272 (1965).
- (8) A. Seres, J. Phys. Radium, 14, 689 (1953).
- (9) F. Hulliger, Structure and Bonding, 4, 83 (1968).
- (10) H. Holseth and A. Kjekshus, J. Less-Common Metals, 16, 472 (1968).
- (11) A. Temperley and M. Lefevre, J. Phys. Chem. Sol., 27, 85 (1966).
- (12) R. Darmon and M. Wintenberger, Bull. Soc. France Miner. Cryst., 89, 213 (1966).
- (13) F. Hulliger, Phys. Lett., 4, 282 (1963).
- (14) S. L. Bennett and R. D. Heyding, Can. J. Chem., 44, 3017 (1966).

SECTION III

PREPARATION AND PROPERTIES OF IRON MONOPHOSPHIDE[#]

by

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ABSTRACT

Fused salt electrolysis and chemical transport have been investigated as means of growing single crystals of FeP suitable for physical measurements. Magnetic susceptibility and electrical resistivity have been measured from 4.2°K to 298°K on crystals grown by these techniques. FeP exhibits metallic behavior throughout this temperature range. Anomalies in the magnetic susceptibility and resistivity curves at about 120°K have been correlated with an ordered antiferromagnetic spiral. The nature of additional anomalies observed at about 30°K has not yet been determined.

INTRODUCTION

The most common method used for the preparation of transition metal phosphides is the direct combination of the elements. The various synthetic techniques for the synthesis of phosphides are summarized in the monograph by Aronsson et al.⁽¹⁾. However, in general, the products are not pure or

[#]This research was sponsored by Wright-Patterson Air Force Base, MAIT, under contract number AF 33(615)-3844

homogeneous and any crystals produced are usually small and of poor quality. Andrieux and Chêne⁽²⁻⁸⁾ first demonstrated that fused salt electrolysis could be used to prepare transition metal phosphides. Wood⁽⁹⁾, Yocom⁽¹⁰⁾, Hsu and co-workers^(11,12) further developed this method. Electrolysis of fused salts appears to have great potential for the production of relatively pure compounds but little has been published concerning its application to the growth of single crystals.

The inability to prepare a well-defined, homogeneous phase of FeP has resulted in conflicting reports concerning its magnetic properties. Chiba⁽¹³⁾ first reported FeP to be paramagnetic with typical Curie-Weiss behavior in the temperature range from 290°K to 900°K. Meyer and Cadeville⁽¹⁴⁾, in a later study, indicated that FeP was ferromagnetic with a Curie point of 215°K. Above the Curie point FeP followed a Curie-Weiss behavior, but with constants differing considerably from those reported by Chiba. In a recent study of transition metal monophosphides, Stein and Walmsley⁽¹⁵⁾ observed essentially temperature independent paramagnetic behavior for FeP. However, their compound was impure. Magnetization data indicated the presence of ferromagnetic impurities and the very low temperature data was apparently affected by localized regions of these impurities. Temperature independent paramagnetic behavior was also observed by Roger and Fruchart^(16,17). However, in a study of the Mössbauer spectra of FeP, Bailey and Duncan⁽¹⁸⁾ observed a change in the iron spectrum from a doublet at room temperature to a broad asymmetric singlet at liquid air temperature (90°K). They were unable to explain this change and no magnetic or crystallographic anomaly has been observed in this region.

The present study was undertaken in order to prepare and characterize pure single crystals of FeP. The technique of electrolysis of fused salts

followed by chemical transport of the products was investigated for the purpose of producing large homogeneous single crystals suitable for physical measurements. Magnetic susceptibility and electrical resistivity measurements were made on well-characterized single crystals.

EXPERIMENTAL

ELECTROLYTIC APPARATUS.

Iron monophosphide single crystals were grown by the electrolysis of sodium metaphosphate-iron (III) fluoride mixtures. The apparatus used for the electrolysis of these fused melts is shown in Figure 2. The assembly is vertically mounted in a split-tube furnace. A mullite tube, with water-cooled brass cap ends sealed by rubber O-rings, provides an enclosed chamber for electrolysis. Gas connections at either end allow the electrolysis to be carried out under an atmosphere of flowing argon. A carbon pedestal centers the carbon crucible in the hot zone of the furnace. The crucible size varied from 1" I.D. by 5" deep to 1-1/2" I.D. by 4" deep. The crucible acts as the anode and a 1/4" centered carbon rod serves as the cathode during electrolysis. The external anode lead wire is connected to the brass plate of the base and the current is conducted through the pedestal to the crucible. The external cathode lead wire is attached to the 1/4" stainless steel rod which supports the center carbon rod. The use of internal wire connection is prohibited by the corrosive nature of the atmosphere in the chamber during electrolysis. The thermocouple for the control of the furnace temperature is placed outside the reaction chamber. This thermocouple is calibrated with respect to a thermocouple placed within the reaction vessel in the absence of a melt.

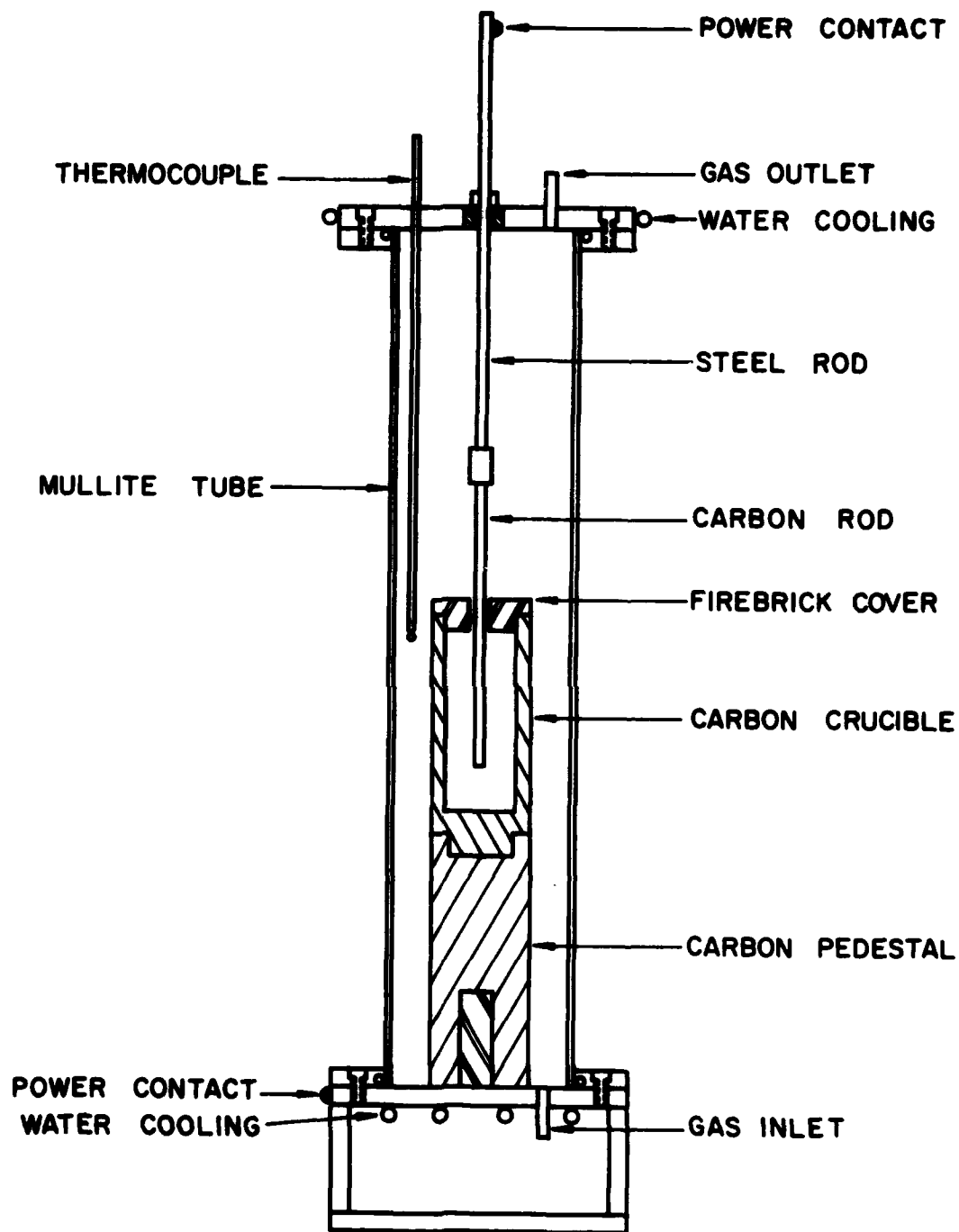


Figure 2 Assembly for Fused Salt Electrolysis

PREPARATION OF THE CRYSTALS.

Ferric (III) fluoride supplied by Ozark-Mahoning or Baker and Adameon, and Fisher Scientific purified grade sodium metaphosphate were used as the melt components. The desired molar proportions of these materials were thoroughly mixed prior to placement in the crucible. The melt was heated to the reaction temperature at the rate of 75°/hr. under an atmosphere of flowing argon and allowed to equilibrate for 1 hr. The centered carbon rod was inserted to a depth of 3/4" and the electrolysis carried out from 12 to 24 hours. A constant current source maintained the desired current. After electrolysis the melt was cooled to room temperature at the rate of 75°/hr. The product was recovered by leaching the melt in hot water or dilute hydrochloric acid. Free carbon was removed by flotation using methylene iodide.

The tubes for chemical transport were prepared in the manner previously described by Kershaw et al.⁽¹⁹⁾. The transport charge was a homogeneous powder of FeP which had been prepared electrolytically. Iodine, ammonium iodide, and a combination of iodine and ammonium iodide were tried as the transporting agents. All transport reactions were carried out in a two-zone furnace with the transport from the hot zone to the cool zone. Initially the charge zone was set at 500°C and the growth zone at 800°C and the tube was heated for two days. This period of back-transport minimizes the number of nucleation sites. The temperatures of the zones were then reset to 800°C for the charge zone and 540°C for the growth zone. The transport was then carried out for periods from one to two weeks. At the end of the transport period, the furnace was shut off and allowed to cool to room temperature. The crystals were removed from the tube and washed with carbon tetrachloride and acetone to remove excess iodine.

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CHEMICAL ANALYSIS.

The sample was ground and dissolved in a mixture of hydrochloric and nitric acid (75:1). The solution was passed through a silver column and titrated with standardized ceric sulfate. Phosphorus was analyzed by reacting the phosphide with a quinquevalent vanadium sulfate solution and reoxidizing the quadrivalent vanadium produced with a standard solution of KMnO_4 .
Anal. Calcd. for FeP : Fe, 64.33; P, 35.67. Found: Fe, 64.17; P, 35.60.

PHYSICAL MEASUREMENTS.

Cell parameters for powder samples were determined with a Norelco diffractometer using monochromatic radiation (AMR-202 focusing monochromator) and a high-intensity copper source. The radiation used was $\lambda(\text{CuK}\alpha_1)$ 1.5405 Å. The values were confirmed by single-crystal analysis using precession X-ray techniques. The observed cell parameters are summarized in Table I.

The magnetic susceptibility was measured with a Faraday balance previously described by Morris et al.⁽²¹⁾. The resistivity was measured using the four-probe technique for the crystals prepared by electrolysis and the van der Pauw technique for the crystals prepared by chemical transport. In the latter case a suitable face of the transported crystal was chosen and a second face was ground and polished parallel to it in order to provide the thin plates necessary for the measurement. Indium leads were attached by means of ultrasonic soldering.

RESULTS AND DISCUSSION

For the preparation of transition metal phosphides by electrolysis, previous investigators⁽²⁻¹²⁾ used a mixture of a transition metal oxide and

TABLE I. X-RAY DATA FOR FeP

<u>Sample</u>	<u>Unit Cell Dimensions (in Å)</u>		
	<u>a</u>	<u>b</u>	<u>c</u>
Electrolysis (Single Crystal)	5.19 ± 0.005	3.099 ± 0.005	5.79 ± 0.005
Electrolysis (Powder)	5.188 ± 0.005	3.097 ± 0.004	5.789 ± 0.005
Chemical Transport (Single Crystal)	5.196 ± 0.006	3.099 ± 0.005	5.792 ± 0.006
Chemical Transport (Powder)	5.189 ± 0.005	3.096 ± 0.004	5.788 ± 0.005
Rundqvist (20)	5.19	3.099	5.79

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sodium metaphosphate. Sodium fluoride or carbonate was added in order to facilitate solution of the metal oxide. This method usually resulted in products of uncertain compositions that were also contaminated by transition metal oxide. In addition, the yields were low as a result of incomplete solution of the metal oxide in the phosphate melt, partial hydrolysis of the fluorides present, and incomplete reduction of the metal complexes present in the melt. However, the use of iron (III) fluoride is preferable since it is readily soluble in sodium metaphosphate. Slow heating under a flowing argon atmosphere permits the removal of moisture without the loss of appreciable fluoride. Low reduction potentials (~ 0.7 v) were sufficient to give the desired monophosphide. White phosphorus deposits, reported as a by-product in the earlier studies, were not observed to form in the electrolysis of the iron (III) fluoride-sodium metaphosphate melt.

The composition of the products obtained from the electrolysis of iron (III) fluoride and sodium metaphosphate was dependent on the phosphorus to iron ratio as well as the reaction temperature. The quality and size of the crystals depends on the current density and reaction time. Single crystals of FeP in the form of needles 1 - 2 mm in length were grown by the electrolysis of a melt containing a phosphorus to iron ratio of 11:1. The reaction temperature was 925°C and a current of 200 mA was used. Currents of less than 200 mA resulted in the growth of many small crystals. Excessive twinning was observed when currents of 400 - 600 mA were used.

Larger crystals of FeP were grown by chemical transport of the product prepared by electrolysis. This starting material was homogeneous and of known stoichiometry. The best transport agent used was iodine at a concentration of 5 mg/cm³. Crystals of FeP with well-defined faces ranging in size to 3 x 3 x 3 mm were grown after transporting for ten days from a

temperature of 800°C to 540°C in a two-zone furnace.

A plot of the magnetic susceptibility vs. temperature for powdered samples of FeP prepared both by electrolysis and by chemical transport is given in Figure 3. It can be seen that there are two separate regions of temperature independent behavior (room temperature to 140°K and 80°K to 55°K) separated by a broad region where the susceptibility decreases with decreasing temperature. The low temperature susceptibility (55°K to liquid helium) is seen to increase with decreasing temperature. From Table II it is clear that the susceptibility was field independent at 77°K and 298°K. However, the susceptibility did become field dependent at 4.2°K.

The observed magnetic behavior is not consistent with the properties reported by Chiba⁽¹³⁾ and by Meyer and Cadaville⁽¹⁴⁾. Although both Stein and Walmsley⁽¹⁵⁾ and Roger and Fruchart⁽¹⁶⁾ report temperature independent Pauli paramagnetic behavior, neither observed the transition in the temperature region from 80°K to 140°K. This transition is consistent, however, with the change in the Mössbauer spectra reported by Bailey and Duncan⁽¹⁸⁾. In addition, Felcher et al.⁽²²⁾ has observed from neutron diffraction measurements that FeP is an antiferromagnetic spiral at liquid nitrogen temperature (77°K), but has no observable spin ordering at room temperature. The Néel temperature has not been determined. The low temperature behavior is consistent with that reported by Stein and Walmsley.

The anomalies in the magnetic behavior are also observed in the electrical measurements. The resistivity, shown in Figure 4, exhibits essentially metallic behavior (3×10^{-7} Ω -cm at 4.2°K to 8×10^{-5} Ω -cm at 360°K). There is an inflection point in the resistivity curve at 120°K. This is consistent with the change observed in the magnetic susceptibility curve shown in

TABLE II. FIELD DEPENDENCE OF THE SUSCEPTIBILITY OF FeP

(in units of 10^{-6} emu/g)

Temperature (°K)	Magnetic Field (K0e)					
	6.25	7.40	8.50	9.25	9.90	10.30
298	3.72	3.74	3.72	3.74	3.74	3.73
77	3.11	3.09	3.08	3.10	3.08	3.09
5	4.57	4.54	4.51	4.52	4.45	4.46

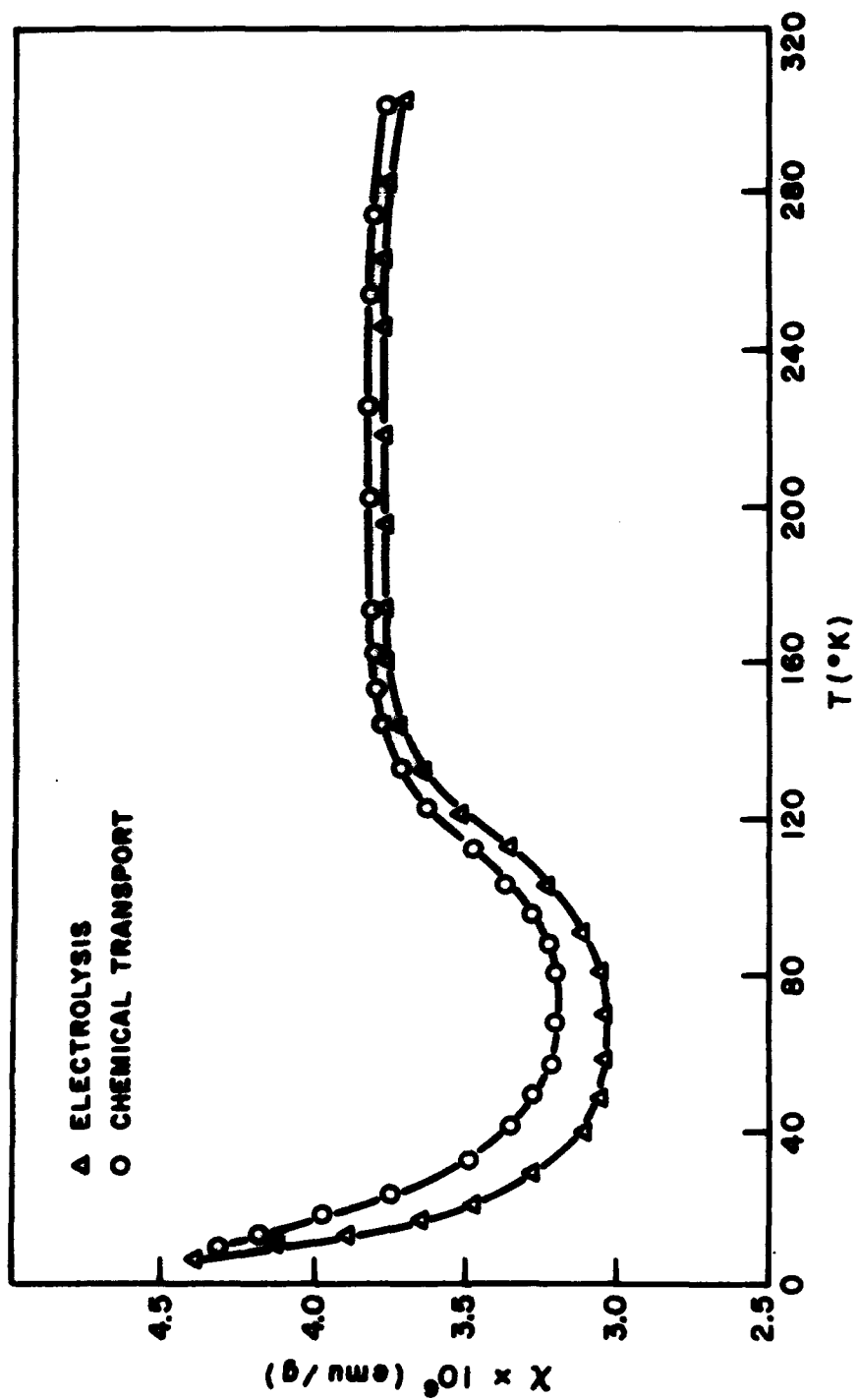


Figure 3 Temperature Dependence of the Susceptibility for FeP

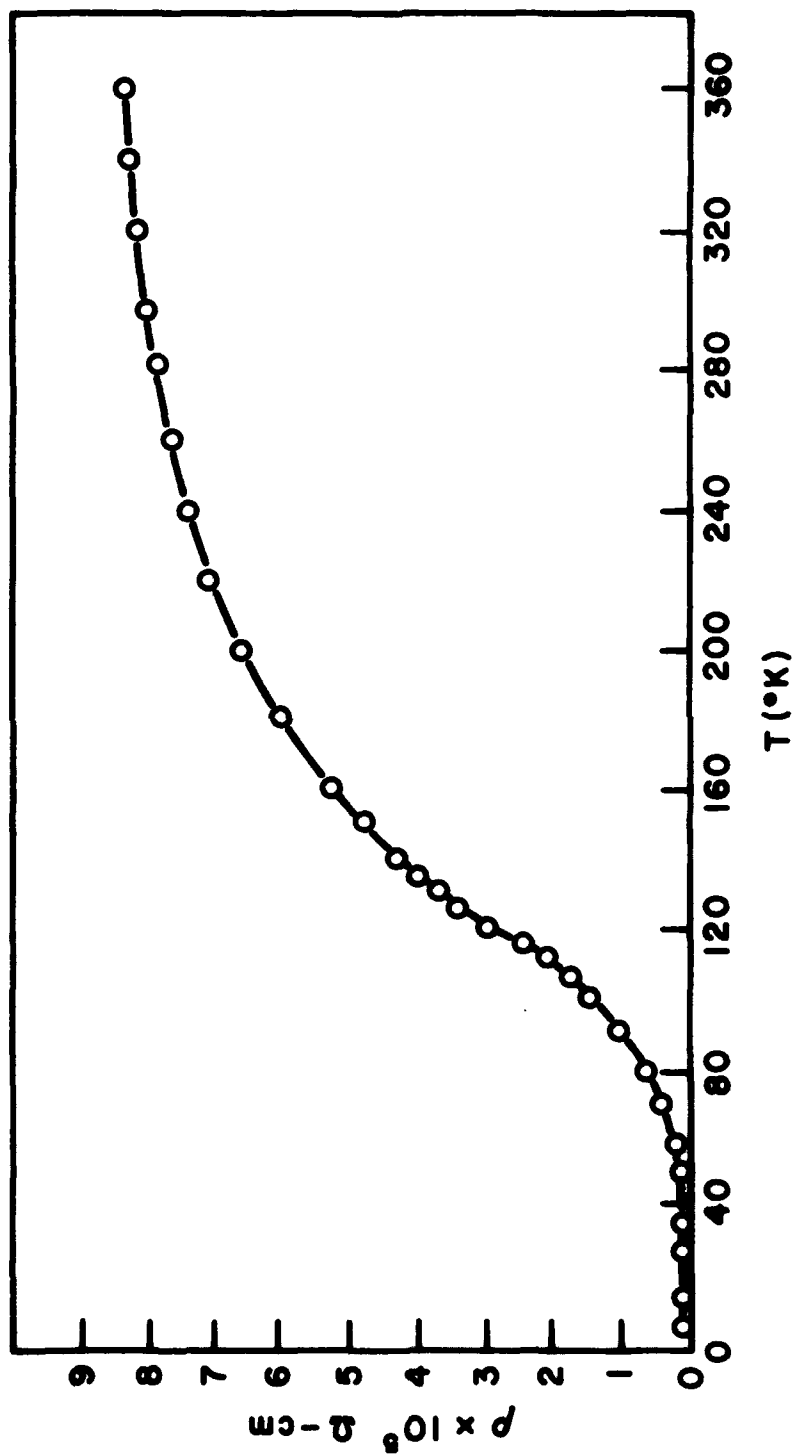


Figure 4 Temperature Dependence of the Resistivity for FeP

Figure 3. The anomalous behavior observed at 120°K for the Mössbauer spectra, magnetic susceptibility and resistivity curves, coincides with the existence of an ordered antiferromagnetic state. It can be seen from Figure 5 that there is a discontinuity in the resistivity at 25°K. This is consistent with anomalies observed in the magnetic behavior. The nature of this transition is unknown but is presently being examined by neutron diffraction.

ACKNOWLEDGMENTS

We wish to thank Mr. Walter Kunnmann of Brookhaven National Laboratory for suggesting the electrolytic technique for the preparation of FeP, and Dr. Gian Felcher of Argonne National Laboratory for the results of the neutron diffraction measurements.

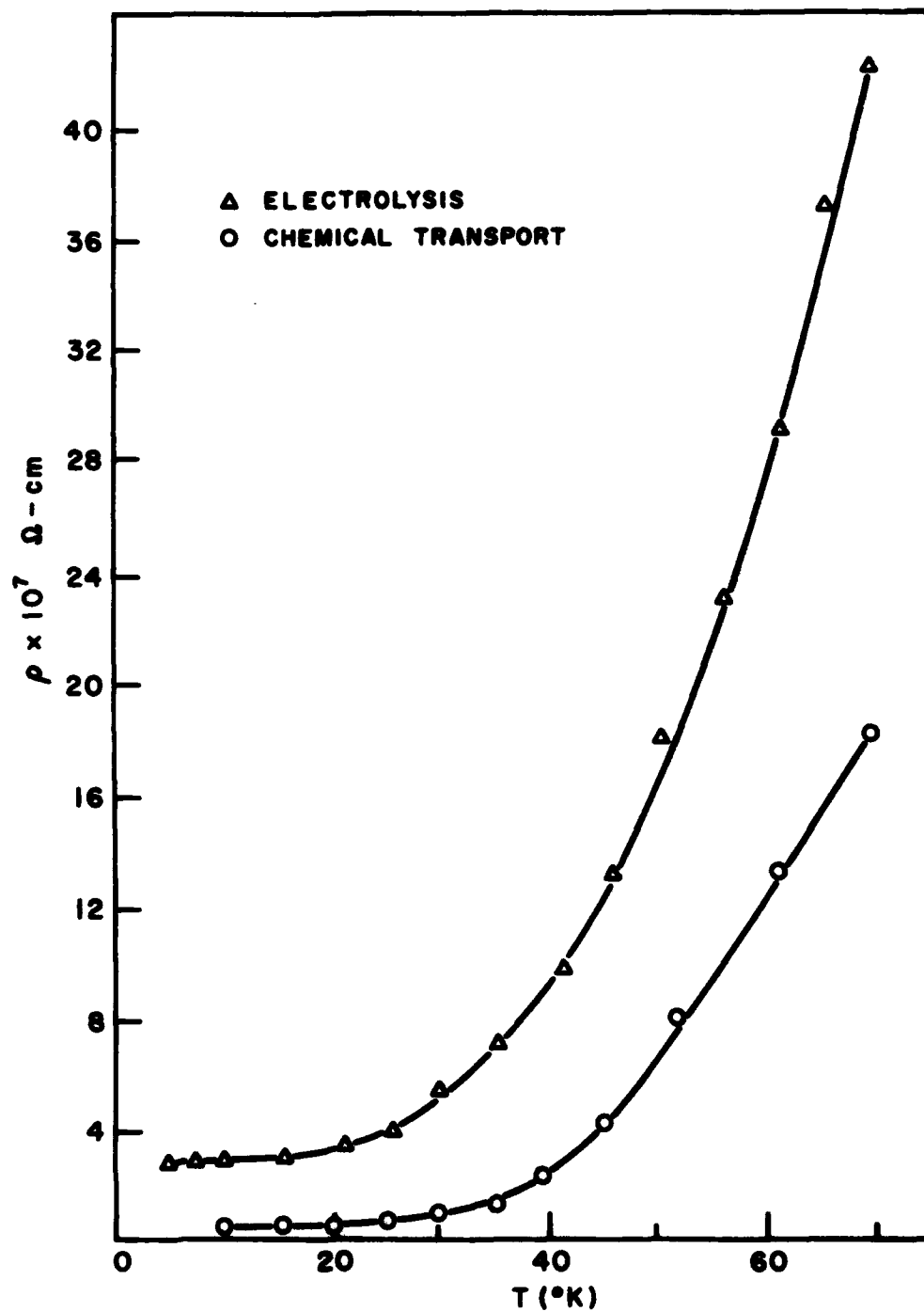


Figure 5 Low Temperature Dependence of the Resistivity for FeP

REFERENCES

- (1) B. Aronsson, T. Lundstrom and S. Rundqvist, "Borides, Silicides and Phosphides," John Wiley & Sons, Inc., New York, 1965.
- (2) J. L. Andrieux, *Rev. Met.*, 45, 49 (1948).
- (3) J. L. Andrieux and M. Chêne, *Compt. Rend.*, 206, 661 (1938).
- (4) J. L. Andrieux and J. Chêne, *ibid.*, 206, 1562 (1938).
- (5) J. L. Andrieux and J. Chêne, *ibid.*, 209, 672 (1939).
- (6) M. Chêne, *ibid.*, 207, 571 (1938).
- (7) M. Chêne, *ibid.*, 208, 1144 (1939).
- (8) M. Chêne, *Ann. Chim.*, 15, 266 (1941).
- (9) D. W. Wood, Ph.D. Thesis, University of Illinois, 1953.
- (10) P. N. Yocum, Ph.D. Thesis, University of Illinois, 1958.
- (11) S. S. Hsu, P. N. Yocum and T. C. C. Cheng, *Interim Report*, Contract No. NS-ori-071(50)-NR 052-341, December 1953 - July 1955.
- (12) S. S. Hsu, P. N. Yocum et al., *Final Report*, *ibid.*, July 1953 - December 1958.
- (13) S. Chiba, *J. Phys. Soc. Jap.*, 15, 581 (1960).
- (14) A. J. P. Mayer and M.-C. Cadaville, *J. Phys. Soc. Jap.*, Suppl. B-1, 17, 223 (1962).
- (15) B. F. Stein and R. H. Walsley, *Phys. Rev.*, 148, 933 (1966).
- (16) A. Roger and R. Fruchart, *Compt. Rend.*, 264, 508 (1967).
- (17) J. Bonnet, R. Fruchart and A. Roger, *Physics Letters*, 26A, 536 (1968).
- (18) R. E. Bailey and J. F. Duncan, *Inorg. Chem.*, 6, 1444 (1967).
- (19) R. Kershaw, M. Vlasse and A. Wold, *Inorg. Chem.*, 6, 1599 (1967).
- (20) S. Rundqvist, *Acta Chem. Scand.*, 16, 287 (1962).
- (21) B. Morris and A. Wold, *Rev. Sci. Instr.*, 39, 1937 (1968).
- (22) G. Falcher, private communication.

SECTION IV

A. GROWTH OF CADMIUM SULFIDE AND ZINC-DOPED CADMIUM SULFIDE SINGLE CRYSTALS.

The knowledge gained from the study of crystal growth by chemical transport can be applied to vapor growth techniques in general. As a result we have grown pure cadmium sulfide crystals from the vapor phase. Successful growth of transparent cadmium sulfide ribbons, with dimensions approximately 12 mm long x 9 mm wide and .2 mm thick, has been achieved.

The design of the furnace used to grow the crystals is shown in Figure 6. The furnace consists of a 12" diameter transite shell which is 46" long. Five inch wide removable sections extend along the entire length of the furnace and terminate 2" from each end. This provides ready access to the individual heating modules. A transite disc having a 2-1/2" diameter central hole is secured at each end of the furnace body. These holes are positioned so as to accommodate a silica muffle.

The heating elements are independently wound, with Kanthal "A" type wire, on a 3" O.D. spiral-grooved Norton core. Two 3/8" stainless steel rods pass through the entire length of the furnace and provide support for the heating element. The temperature control unit for each zone is a West J P C controller. Sensing-thermocouples are located in the bore of the furnace alongside of the main tube. Cerafelt pads, comparable in size with the inside diameter of the furnace and having a 3" diameter center hole, are placed against each of the heating element ends and serve as insulating partitions. Heat losses that develop through adjustable air gaps between the zones provide the means of producing a step-type temperature gradient. A typical temperature profile is shown in Figure 7.

The tube furnace contains a 55 mm silica muffle in which crystal growth

LEGEND

	FIREBRICK		CERAFELT		HEATERS
	TRANSITE		TRANSITE		

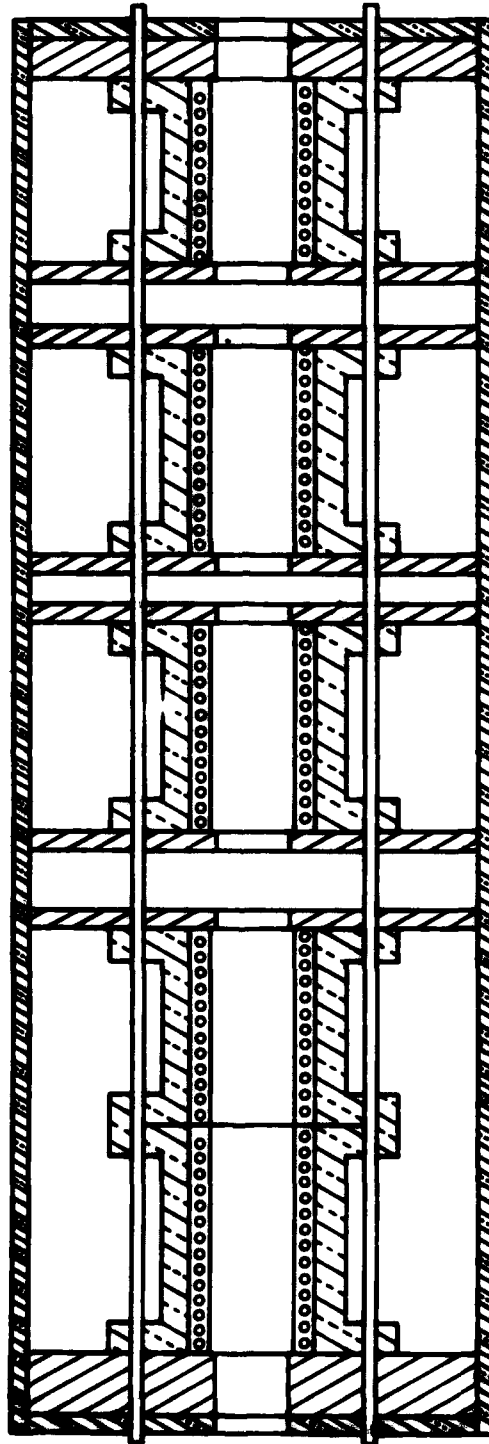


Figure 6 Four Zone Vapor Transport Furnace

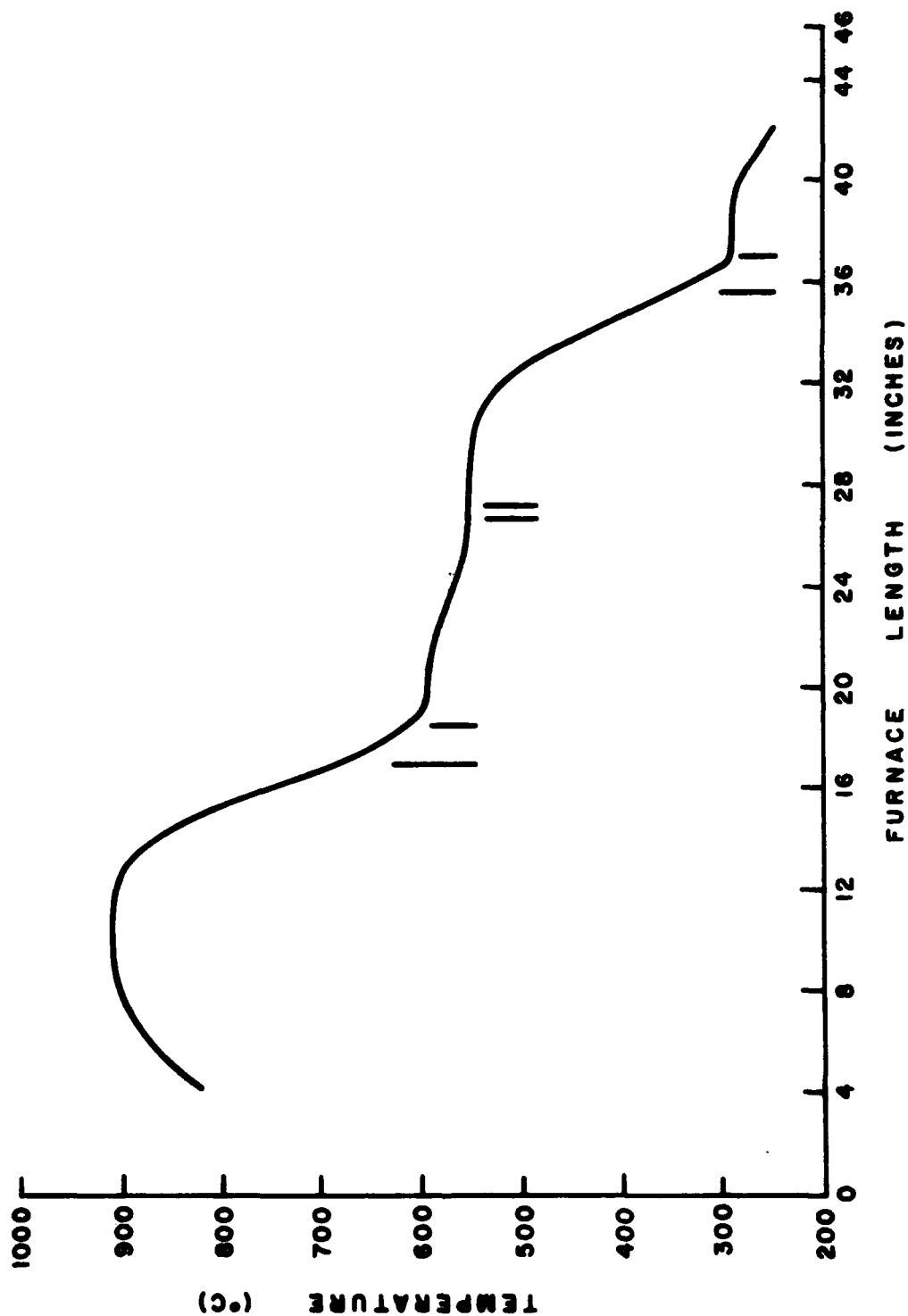


Figure 7 Temperature Profile for Growth of CdS Crystals

occure, Figure 8. There are three 20 mm diameter silica tubes placed within the muffle which allow for the independent volatilization and transport of each element to the growth site. The end caps have R.T.V. 511 silicone gas-kets which prevent leakage of the carrier gas. The carrier gas consists of 85% argon, 15% hydrogen and is first passed through a "Decxo" catalytic purifier to remove oxygen. The gas then enters a drierite column to remove traces of moisture. In order to remove hydrocarbon impurities, the gas is first passed through a Dry Ice acetone cold trap filled with molecular sieve and then through four 12 mm diameter silica tubes each filled with molecular sieve beads which are heated to 300°C. The preheated purified carrier gas then enters each of the inner silica tubes as well as the muffle. This is also shown in Figure 8.

For the growth of CdS crystals, the vapor pressures of cadmium and sulfur are controlled by the temperature of their respective zones. The carrier gas mixture of 85% argon and 15% hydrogen is used to carry both the cadmium and sulfur vapors to the growth zone. Approximately two grams of each element are placed in separate alundum boats. The elements are then inserted into the inner tubes in such positions that their vapor pressures are each 100 mm Hg (327°C for sulfur and 611°C for cadmium). The growth zone temperature is maintained at 1000°C and the carrier gas rate is adjusted for optimum crystal growth. The crystal surfaces were free of striations and the resistivity of these crystals, measured at 23°C, was $2 \times 10^6 \Omega\text{-cm}$. In addition, white, transparent plates of pure zinc sulfide, measuring 3 mm x 1 mm x 0.1 mm have also been grown. Mixed crystals of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ were obtained although they were smaller and thinner than the CdS crystals. However, they were of the same fine quality as the CdS plates. Spectrographic analysis of the crystals indicated that they contained up to 1% zinc by weight. A noticeable greenish

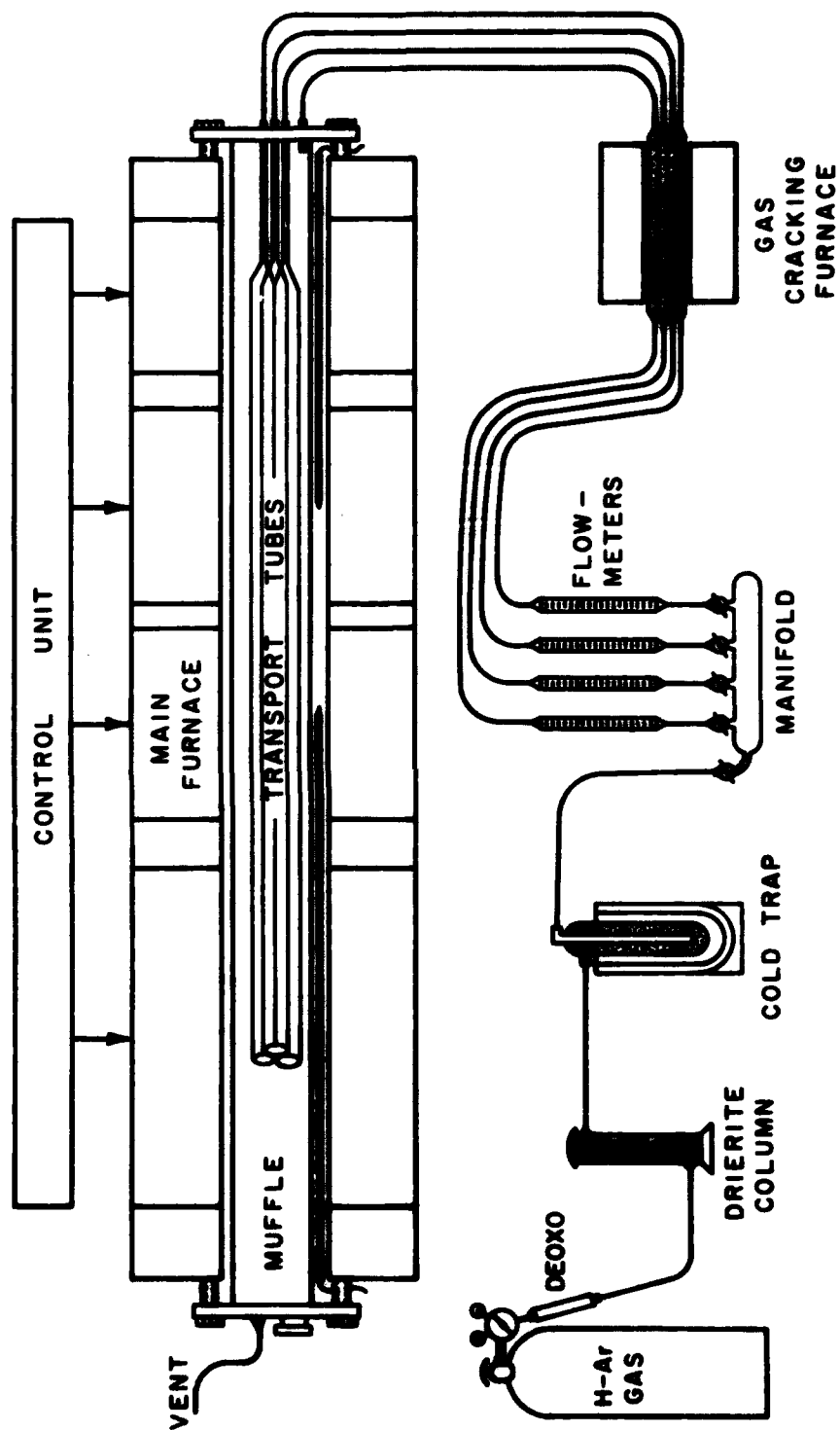


Figure 8 Gas Train for Growth of Zn-doped CdS Crystals

tint can be detected in crystals containing 1% by weight of zinc. The conditions used for the growth of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ crystals are summarized in the following Table.

CONDITIONS FOR THE GROWTH OF $\text{Cd}_{1-x}\text{Zn}_x$ CRYSTALS

Compound	Element	Vapor Pressure	Gas Flow Rate	Nucleation Temperature	Crystal Growth Temperature
CdS	Cd	100 mm	40 ml/min H-Ar	1000°C	910°C
	S	40 mm	40 ml/min H-Ar		
ZnS	Zn	40 mm	30 ml/min H-Ar	1000°C	930°C
	S	40 mm	30 ml/min H-Ar		
$\text{Cd}_{1-x}\text{Zn}_x\text{S}$	Cd	40 mm	40 ml/min H-Ar	1000°C	920°C
	S	40 mm	40 ml/min H-Ar		
	Zn	10 mm to 100 mm	30 ml/min H-Ar		

B. ELECTRICAL PROPERTIES OF CADMIUM SULFIDE PLATELETS.

Resistivity measurements of the cadmium sulfide crystals were made by conventional four-probe technique. The leads were attached by the use of ultrasonic soldering using indium as the solder. The resistivity of cadmium sulfide platelets grown by the technique described in section A was $2 \times 10^6 \Omega\text{-cm}$. A number of the platelets were then heated in a sealed silica tube at 800°C and quenched in cold water. The resistivity of these crystals was reduced to 219.3 $\Omega\text{-cm}$. On the addition of 1% by weight of excess cadmium

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powder to the crystals and heating the mixture in an evacuated silica tube for 64 hours at 800°C, the resistivity was further reduced to $8.17 \times 10^{-3} \Omega\text{-cm}$. Samples of these crystals are being sent to Wright-Patterson for further evaluation.

SECTION V

FUTURE RESEARCH

The techniques of electrolysis, chemical and vapor transport have been developed to a sufficient degree in our laboratory that a large number of new compounds can now be grown as well-defined single crystals. These include II-VI compounds and transition metal phosphides and arsenides. Physical studies on many of these compounds will be continued including X-ray, transport and magnetic measurements. The results, as well as samples of crystals, will be forwarded to interested parties at Wright-Patterson Air Force Base.

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4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Summary Technical Report, 1 May 1967 - 30 April 1969		
5. AUTHOR(S) (Last name, first name, initial) Wold, Aaron		
6. REPORT DATE July 1969	7a. TOTAL NO. OF PAGES 34	7b. NO. OF REFS 36
8a. CONTRACT OR GRANT NO. AF 33(615)-3844 8. PROJECT NO. 7371	8b. ORIGINATOR'S REPORT NUMBER(S)	
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13. ABSTRACT Single crystals of FeP , Fe_2P , CoAs_2 and FeAs_2 were grown by either electrolysis of fused salts or chemical transport. Of these four compounds prepared to date, extensive studies have been carried out on well-characterized crystals of FeP . This compound exhibits metallic behavior throughout the temperature range of 4.2°K to 298°K . Anomalies in the magnetic susceptibility and resistivity curves at about 120°K have been correlated with an ordered antiferromagnetic spiral. The other compounds have been chemically analyzed and their electrical and magnetic properties are being characterized. In addition, crystals of cadmium sulfide have been grown from the vapor phase with dimensions 12 mm long x 9 mm wide x 0.2 mm thick. The resistivity of these crystals was found to be $2 \times 10^6 \text{ ohm-cm}$ at room temperature. On heating these crystals to 800°C for 4 hours and quenching to room temperature, the resistivity was found to be 219.3 ohm-cm . Samples of these crystals will be delivered to Dr. P. Hemenger at Wright-Patterson. (This abstract has been approved for public release and sale; its distribution is unlimited.)		

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