JOURNAL OF SOLID STATE CHEMISTRY, 1, 82–87 (1969)

Preparation and Properties of Iron Monophosphide†

DAVID BELLAVANCE, MARCUS VLASSE, BERNARD MORRIS, AND AARON WOLD

Departments of Chemistry, Physics, and Division of Engineering, Brown University,
Providence, Rhode Island 02912

Received December 13, 1968

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 4.2K to 298K on crystals grown by these techniques. FeP exhibits metallic behavior throughout this temperature range. Anomalies in the magnetic susceptibility and resistivity curves at about 120K have been correlated with an ordered antiferromagnetic spiral. The nature of additional anomalies observed at about 30K 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 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 *et al.* (*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 290K to 900K. Meyer and Cadeville (*14*), in a later study, indicated that FeP was ferromagnetic with a Curie point of 215K. 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 (90K). 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 Fig. 1. The assembly is vertically mounted in a split-tube

---

† This research was sponsored by Wright-Patterson Air Force Base, MAYT, under contract number AF 33(615)-3844.

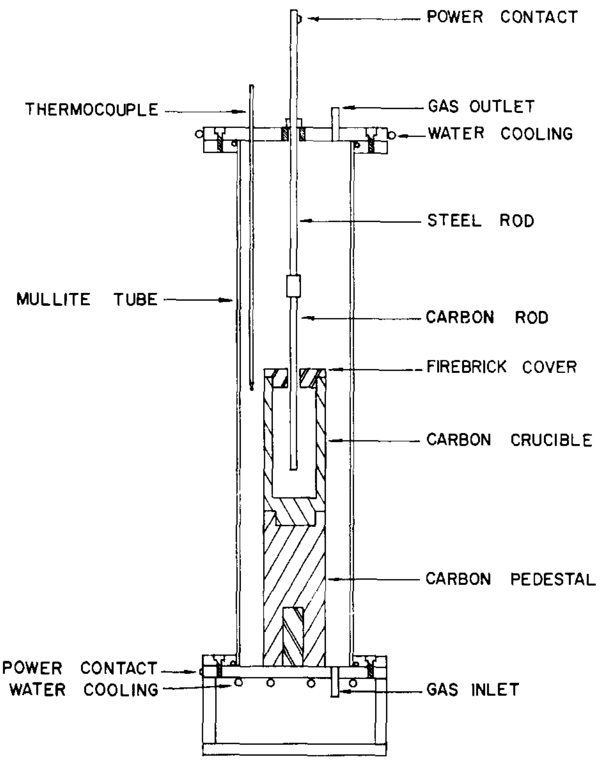

FIG. 1. Assembly for fused salt electrolysis.

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 in. i.d. by 5 in. deep to $1\frac{1}{2}$ in. i.d. by 4 in. deep. The crucible acts as the anode and a $\frac{1}{4}$-in. 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 $\frac{1}{4}$-in. 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.

Preparation of the Crystals

Ferric (III) fluoride supplied by Ozark-Mahoning or Baker and Adamson, 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 $\frac{3}{4}$ in. and the electrolysis carried out from 12 to 24 hr. 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 500C and the growth zone at 800C and the tube was heated for 2 days. This period of back-transport minimizes the number of nucleation sites. The temperatures of the zones were then reset to 800C for the charge zone and 540C for the growth zone. The transport was then carried out for periods from 1 to 2 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.

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 monochrometer) and a high-intensity copper source. The radiation used was $\lambda(CuK_{\alpha_1})$ 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 ultra-sonic 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 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 925C and a current of 200 mA was used. Currents of less than 200 mA resulted in the

TABLE I

X-RAY DATA FOR FeP

Sample	Unit cell dimensions (in Å)		
	a	*b*	*c*
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	5.786 ± 0.005
Rundqvist (20)	5.19	3.099	5.79

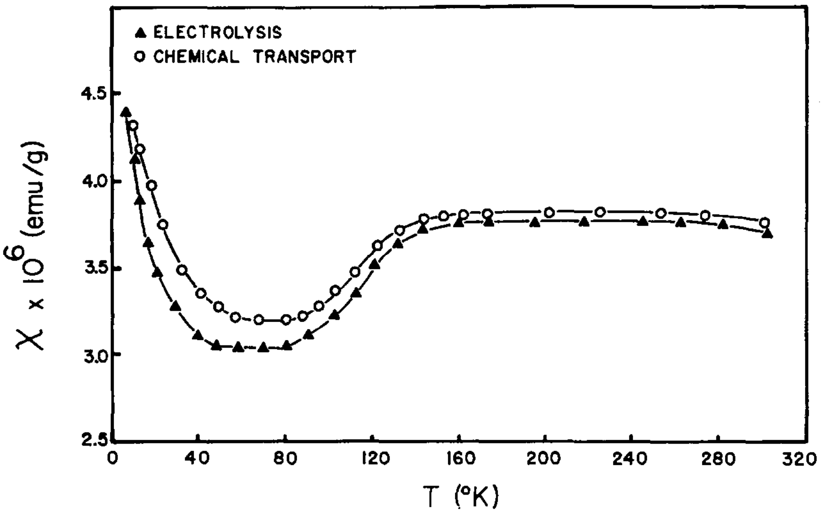

FIG. 2. Temperature dependence of the susceptibility for FeP.

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/cm^3. Crystals of FeP with well-defined faces ranging in size to 3 × 3 × 3 mm were grown after transporting for 10 days from a temperature of 800C to 540C 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 Fig. 2. It can be seen that there are two separate regions of temperature independent behavior (room temperature to 140 and 80 to 55K) separated by a broad region where the susceptibility decreases with decreasing temperature. The low temperature susceptibility (55K to liquid helium) is seen to increase with decreasing temperature. From Table II it is clear that the susceptibility was field independent at 77 and 298K. However, the susceptibility did become field dependent at 4.2K.

The observed magnetic behavior is not consistent with the properties reported by Chiba (*13*) and by Meyer and Cadeville (*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 to 140K. 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 (77K), but has no observable spin

TABLE II

FIELD DEPENDENCE OF THE SUSCEPTIBILITY OF FeP (IN UNITS OF 10^{-6} emu/g)

	Magnetic field (kOe)					
Temperature (K)	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

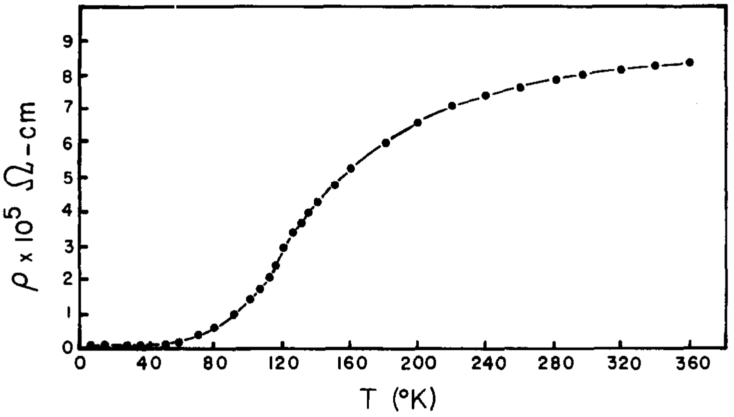

FIG. 3. Temperature dependence of the resistivity for FeP.

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 Fig. 3, exhibits essentially metallic behavior (3×10^{-7} Ω-cm at 4.2K to 8×10^{-5} Ω-cm at 360K). There is an inflection point in the resistivity curve at 120K. This is consistent with the change observed in the magnetic susceptibility curve shown in Fig. 2. The anomalous behavior observed at 120K for the Mössbauer spectra, magnetic susceptibility and resistivity curves

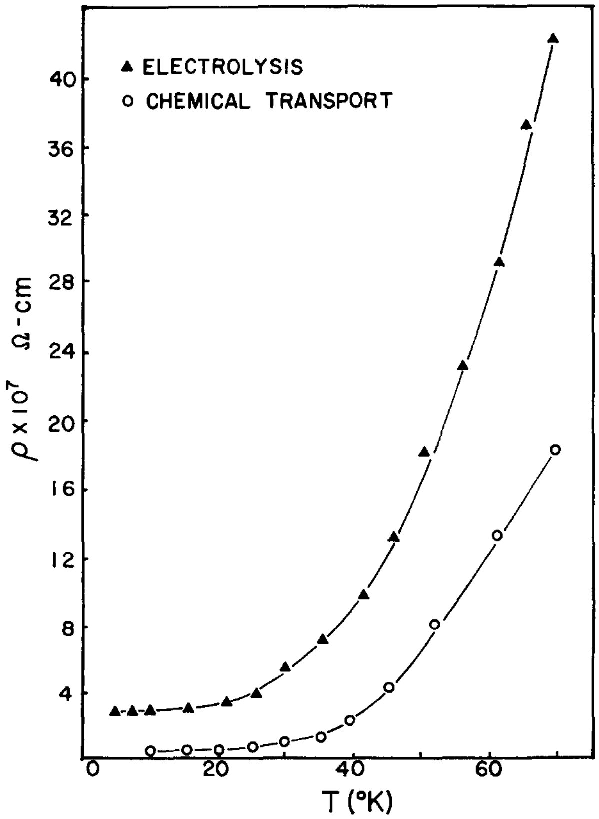

FIG. 4. Low temperature dependence of the resistivity for FeP.

coincides with the existence of an ordered antiferromagnetic state. It can be seen from Fig. 4 that there is a discontinuity in the resistivity at 25K. 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.

References

1. B. Aronsson, T. Lundstrom, and S. Rundqvist, "Borides, Silicides and Phosphides," Wiley, 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, *Compt. Rend.* **206**, 1562 (1938).
5. J. L. Andrieux and J. Chêne, *Compt. Rend.* **209**, 672 (1939).
6. M. Chêne, *Compt. Rend.* **207**, 571 (1938).
7. M. Chêne, *Compt. Rend.* **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. Yocom, Ph.D. Thesis, University of Illinois (1958).
11. S. S. Hsu, P. N. Yocom, and T. C. C. Cheng, *Interim Report*, Contract No. N6-ori-071(50)-NR 052–341, December 1953–July 1955.
12. S. S. Hsu, P. N. Yocom *et al.*, *Final Report*, Contract No. N6-ori-071(50)-NR 052–341, July 1953–December 1958.
13. S. Chiba, *J. Phys. Soc. Jap.* **15**, 581 (1960).
14. A. J. P. Meyer and M.-C. Cadeville, *J. Phys. Soc. Jap. Suppl. B*-1 **17**, 223 (1962).
15. B. F. Stein and R. H. Walmsley, *Phys. Rev.* **148**, 933 (1966).
16. A. Roger and R. Fruchart, *Compt. Rend.* **264**, 508 (1967).
17. J. Bonnert, 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. Inst.* (to be published).
22. G. Felcher (private communication).