

Preparation and Properties of $\text{Fe}_2\text{P}^\dagger$

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The system $\text{Fe}_{2-\delta}\text{P}$, with the Fe_2P structure, has been studied where δ varies from 0 to 0.10. The bulk magnetic properties of these phases have been investigated and correlated with deviations in stoichiometry. Fe_2P and $\text{Fe}_{1.91}\text{P}$ have Curie temperatures of 225 and 223°K, respectively; the observed magnetic moment of these materials varied from 1.28 $\mu\text{B}/\text{Fe}$ atom for $\text{Fe}_{1.91}\text{P}$ to 1.10 $\mu\text{B}/\text{Fe}$ atom for Fe_2P . The electrical resistivity of single crystal $\text{Fe}_{1.91}\text{P}$ was measured from 80 to 360°K. Metallic behavior was observed throughout this temperature range. A break in the resistivity curve occurred at 220°K and coincided with the abrupt change in the magnetization curve.

Introduction

The physical properties of diiron phosphide, Fe_2P , have been the subject of many investigations in recent years (1-9). The crystal structure has been determined and refined by Rundqvist and Jellinek (1). Chiba (3) has determined from high temperature susceptibility data that Fe_2P is ferromagnetic with a paramagnetic Curie temperature of 478°K. However, there is considerable disagreement in the reported Curie points and magnetic moments (2-6). The Curie temperature for Fe_2P was reported to be 353°K by LeChatelier and Wologdine (2), 306°K by Chiba (3), and 266°K by Meyer and Cadeville (4, 5). The value of the magnetic moment has varied from 0.85 μB per iron atom reported by Chiba (3) to 1.32 μB per iron atom observed by Meyer and Cadeville (4, 5). Fruchart et al. (6) have investigated the magnetic properties of the solid solutions M_2P ($\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co},$ and Ni) and also confirmed the results of Meyer and Cadeville. The discrepancies in the magnetic properties of Fe_2P have made it difficult to interpret the Mössbauer spectra of this material (7-9).

Meyer and Cadeville (4, 5) also have prepared nonstoichiometric $\text{Fe}_{2-\delta}\text{P}$. This material was reported to have a Curie point of 266°K which is the same as Fe_2P . However, the magnetic moment was

reduced to only 1.07 μB per iron atom. In addition, Fruchart et al. (6) reported considerable variation in the magnetic moment with slight deviations in the stoichiometry. Meyer and Cadeville (4, 5) and Fruchart et al. (6) were the first to report the existence of a range of stoichiometry for Fe_2P . The existence of a range in stoichiometry had also been observed for the systems Mn_2P (10) and Ni_2P (10) which are isostructural with Fe_2P , and for Co_2P (11) which has a structure closely related to Fe_2P . However, there has been no investigation in which X-ray and chemical analysis were both used to determine the homogeneity range for Fe_2P . Therefore, this study was undertaken to investigate the properties of stoichiometric Fe_2P as well as to study the effect of deviations of stoichiometry on the magnetic and electrical properties.

Experimental Section

Preparation of Samples

Two different synthetic techniques were used to prepare the samples for this investigation, namely, direct combination of the elements and fused salt electrolysis. For the direct combination of the elements, predetermined amounts of freshly reduced iron (Gallard-Schlesinger, 99.999%) and red phosphorus (Gallard-Schlesinger, 99.99%) were sealed in evacuated silica tubes and heated for 2 days at 900°C in a pressure bomb. An external pressure of 300-400 psi of argon was maintained on the tubes throughout the initial reaction. The heating and

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TABLE I
CHEMICAL AND X-RAY ANALYSIS OF SAMPLES PREPARED BY DIRECT COMBINATION OF THE ELEMENTS

Sample Number	Fe/P of Reactants	% Fe	Chemical Analysis			X-Ray Analysis Cell Dimensions (Å)	
			% P	Fe/P	Phases	<i>a</i>	<i>c</i>
1	2.00	78.21	21.39	2.02	Fe ₂ P	5.868 ± 0.003	3.458 ± 0.002
2	1.97	77.92	21.93	1.97	Fe ₂ P	5.868 ± 0.002	3.458 ± 0.002
3	1.95	77.79	22.05	1.96	Fe ₂ P	5.867 ± 0.004	3.458 ± 0.003
4	1.90	77.58	22.48	1.91	Fe ₂ P + FeP	5.868 ± 0.003	3.459 ± 0.002
—	—	78.29 ^a	21.72	2.00	Fe ₂ P (1)	5.685	3.456

^a Calculated for Fe₂P.

cooling cycles were programmed at 20°/hr during the first heating. The sintered product was then broken up to a powder by shaking the tube and then the sample was reheated at 900°C for 2 days. Finally, the product was ground in an agate mortar and pestle, sealed in an evacuated silica tube and heated a third time at 900°C for 2–4 days. The repeated grindings and heat treatments were necessary to ensure homogeneity of the final product. Table I summarizes the results of these sample preparations.

The technique of fused salt electrolysis has previously been described by Bellavance et al. (12). In this study, fused melts composed of anhydrous iron(III) fluoride (Ozark-Mahoning Co.) and purified sodium metaphosphate (Fisher Scientific) were electrolyzed in carbon crucibles. The electrolyses were carried out in the temperature range 900–1050°C using a current of 400 mA. The product was removed from the melt by leaching with dilute hydrochloric acid. Magnetic separation removed the product from free carbon. Some samples were also ground in an agate mortar and pestle and annealed in sealed, evacuated silica tubes at 900°C

for 1 week. The results of samples prepared by fused salt electrolysis are summarized in Table II.

Chemical Analysis

For the determination of iron, the sample was ground to a powder and dissolved in a mixture of hydrochloric and nitric acid (75:1). After boiling to near dryness, the solution was fumed several times with concentrated H₂SO₄ to remove the nitrates present. The precipitate was redissolved by the addition of hot dilute hydrochloric acid. Finally, the solution was passed through a silver reductor column and titrated with standardized ceric sulfate.

Total reducing power was determined by reacting the phosphide with vanadium(V) sulfate solution and reoxidizing the vanadium(IV) produced with a standard solution of ceric sulfate. The phosphorus content was calculated from the total reducing power by difference. The results of the chemical analyses are summarized in Tables I and II.

Physical Measurements

Cell parameters for powder samples were determined with a Norelco diffractometer using mono-

TABLE II
PREPARATION AND ANALYSIS OF SAMPLES PREPARED BY FUSED SALT ELECTROLYSIS

Sample Number	Melt Components			Temperature, (°C)	Chemical Analysis			Cell Dimensions (Å)	
	FeF ₃ (g)	NaPO ₃ (g)	P/Fe		% Fe	% P	Fe/P	<i>a</i>	<i>c</i>
5	10	15	1.67	900	77.51	22.51	1.91	5.870 ± 0.003	3.458 ± 0.002
6 ^a	8	12	1.67	1050	77.44	22.52	1.91	5.864 ± 0.004	3.456 ± 0.003
7	10	15	1.67	900	77.39	22.45	1.91	5.865 ± 0.003	3.456 ± 0.002
8	10	20	2.22	900	77.30	22.56	1.90	5.867 ± 0.003	3.458 ± 0.002

^a Annealed.

chromatic radiation (AMR-202 focusing monochrometer) and a high-intensity copper source. The radiation was $\lambda(\text{CuK}\alpha_1)1.5405 \text{ \AA}$. The diffractometer was calibrated relative to a silicon standard. Cell parameters for the different samples are summarized in Tables I and II. Long exposure film photographs were also taken with a Debye-Scherrer camera in order to determine the limit of the $\text{Fe}_2\text{P}/(\text{Fe}_2\text{P} + \text{FeP})$ phase boundary. The radiation used was $\lambda(\text{CrK}\alpha_1)2.2896 \text{ \AA}$.

The magnetic measurements were made with a vibrating sample magnetometer (P.A.R. model FM-1). The magnetometer was calibrated relative to a sample of high purity nickel rod (Jarrell-Ash). Temperature was measured with a pair of copper-constantan thermocouples soldered to the outside of the sample chamber within $\frac{1}{4}$ in. of the sample. All samples were powdered and mounted in delrin sample holders.

Four-probe resistivity measurements were made on the single crystals prepared by fused salt electrolysis. Indium leads were attached by ultrasonic soldering techniques.

Results and Discussion

Samples with a nominal composition varying from Fe_2P to $\text{Fe}_{1.90}\text{P}$ were prepared by direct combination of the elements in sealed, evacuated silica tubes. Table I summarizes the results of chemical and X-ray analyses for these samples. The

chemical analysis of the products is consistent with the starting ratio of the reactants and the calculated cell parameters are in good agreement with the values for Fe_2P reported by Rundqvist and Jellinek (1). It can be seen from Table I that a single phase with the Fe_2P structure exists between the compositions Fe_2P to $\text{Fe}_{1.96}\text{P}$. At the composition $\text{Fe}_{1.90}\text{P}$, X-ray analysis indicated the presence of a two-phase mixture Fe_2P and FeP .

As can be seen from Table II, material with the formula $\text{Fe}_{1.90}\text{P}$ can be prepared by the fused salt electrolysis of a melt with an iron to phosphorus ratio of 2.2:1. Long exposure X-ray photographs of this material gave only lines which could be indexed on the Fe_2P structure. $\text{Fe}_{1.90}\text{P}$ appears to be the lower limit of stoichiometry for the Fe_2P structure that can be prepared from the electrolysis of fused salts. Electrolysis of a fused melt with an iron to phosphorus ratio of 2.4:1 at 900°C resulted in the formation of a two-phase product of Fe_2P and FeP .

Magnetization versus temperature curves for a stoichiometric sample of Fe_2P and a nonstoichiometric sample of $\text{Fe}_{1.91}\text{P}$ prepared by electrolysis are shown in Fig. 1. In both cases the value of the magnetic field was 100 Oe. The prominent feature of both curves is the sharp break in the magnetization at about 200°K . The positive paramagnetic Curie temperature of 478°K reported by Chiba, from susceptibility data to 1100°K , indicates this transition is ferromagnetic rather than ferrimagnetic in

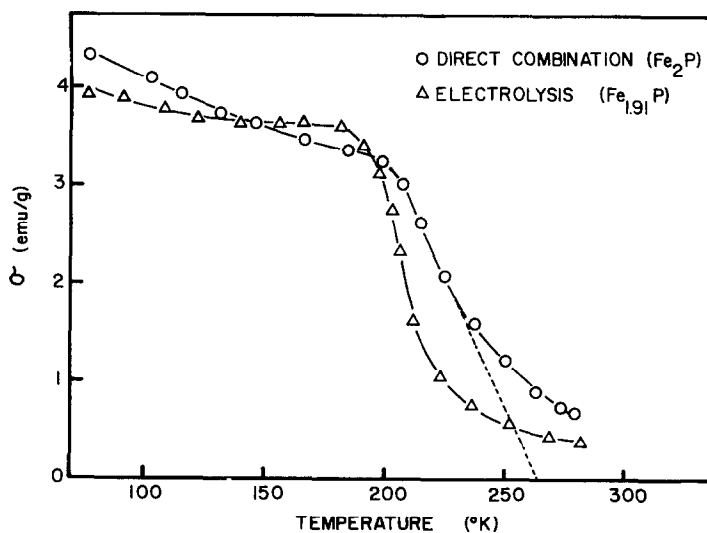


FIG. 1. Magnetization versus temperature for Fe_2P prepared by direct combination and $\text{Fe}_{1.91}\text{P}$ prepared by fused salt electrolysis.

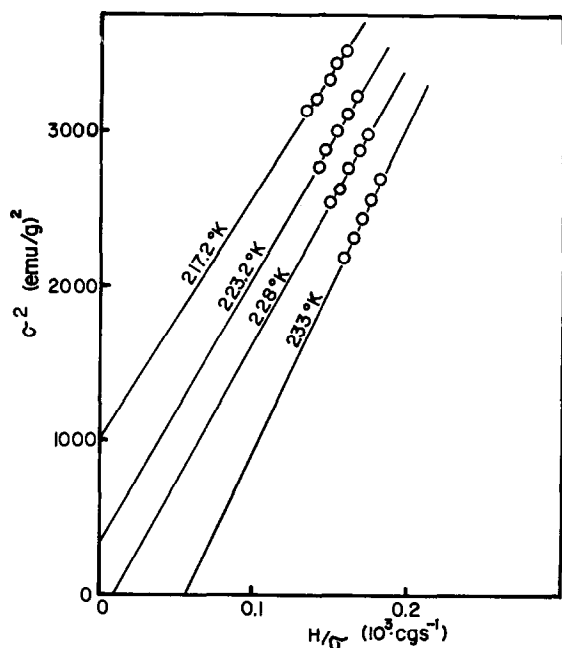


FIG. 2. Isotherms of σ^2 versus H/σ for Fe_2P prepared by direct combination.

nature. The broad tail in the magnetization curve, particularly in the case of the stoichiometric Fe_2P , makes the determination of the Curie temperature difficult. Simple extrapolation of the upper portion of the curve to the temperature axis (dashed line in Fig. 1) gives an intercept of 268°K which is in good agreement with the value reported by Meyer and Cadeville (4, 5). The extrapolation method is believed to give high values for the Curie temperature particularly where broad magnetization curves are used, and inflection points are also difficult to determine.

An alternative method for the determination of the Curie point was proposed by Belov and Goryag (13) and was successfully used by Kouvel and Fisher (14) in the examination of nickel near its Curie point. This technique involves plotting isotherms of σ^2 versus H/σ . The isotherm passing through the origin is defined as the Curie point. Figure 2 shows this type of plot for the sample of Fe_2P . From this plot, the Curie point for Fe_2P was observed to be $226 \pm 2^\circ\text{K}$. Similar Curie points of $225 \pm 2^\circ\text{K}$ were also observed for $\text{Fe}_{1.97}\text{P}$ and $\text{Fe}_{1.96}\text{P}$ using this technique.

It can be seen in Fig. 1 that the magnetization curve for the nonstoichiometric $\text{Fe}_{1.91}\text{P}$ prepared by electrolysis is much sharper than that observed for Fe_2P . A Curie temperature of $223 \pm 2^\circ\text{K}$ for the $\text{Fe}_{1.91}\text{P}$ samples was determined from isothermal plots of σ^2 versus H/σ . This is in close agreement with the value observed for the compositions prepared by direct combination of the elements. The Curie points for all materials are summarized in Table III.

The similar Curie temperatures for the stoichiometric and nonstoichiometric samples indicate that there is little effect on the strengths of the interactions by removing 5% of the iron atoms. It is possible that differences in the shapes of the magnetization curves may be a result of the different preparative techniques and subsequent differences in homogeneity of the samples rather than deviations from stoichiometry. However, there was no evidence in the X-ray patterns for a range of homogeneity within the samples. The X-ray peaks for both stoichiometric and nonstoichiometric samples were equally sharp.

The stoichiometric and nonstoichiometric materials are magnetically hard and do not saturate at

TABLE III

MAGNETIC PARAMETERS OF SAMPLES PREPARED BY DIRECT COMBINATION OF THE ELEMENTS AND FUSED SALT ELECTROLYSIS

Sample	1	2	3	5	6	7
					Annealed	
Method of Preparation ^a	D.C.	D.C.	D.C.	E	E	E
Composition	Fe_2P	$\text{Fe}_{1.97}\text{P}$	$\text{Fe}_{1.96}\text{P}$	$\text{Fe}_{1.91}\text{P}$	$\text{Fe}_{1.91}\text{P}$	$\text{Fe}_{1.91}\text{P}$
T_c ($^\circ\text{K}$)	226 ± 2	225 ± 2	225 ± 2	226 ± 2	223 ± 2	223 ± 2

^a D.C. = Direct combination of the elements; E = fused salt electrolysis.

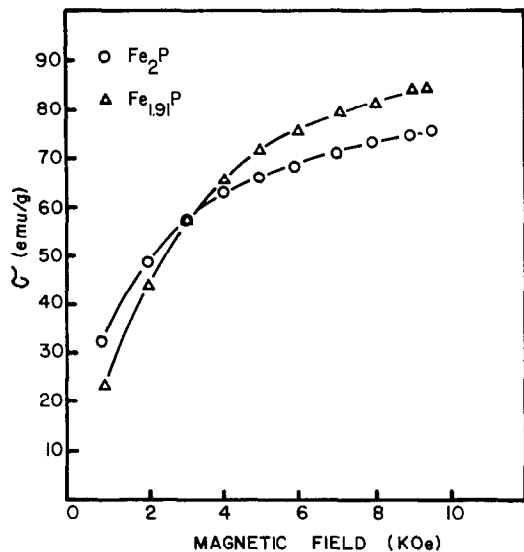


FIG. 3. Field dependence of the magnetization at 4.2°K for Fe₂P and Fe_{1.91}P.

9.5 kOe and 4.2°K (Fig. 3). An approximate value of the saturation magnetization can be obtained by plotting 4.2°K magnetization data as a function of $1/H$ and extrapolating to $1/H = 0$. Curves for Fe₂P and Fe_{1.91}P are shown in Fig. 4. Lack of high-field data makes the absolute value of the saturation moment uncertain, but there is a definite difference between the two samples. The values of $1.10\mu\text{B}/\text{Fe}$ atom for Fe₂P and $1.28\mu\text{B}/\text{Fe}$ atom for Fe_{1.91}P observed in this study are given in Table IV. The

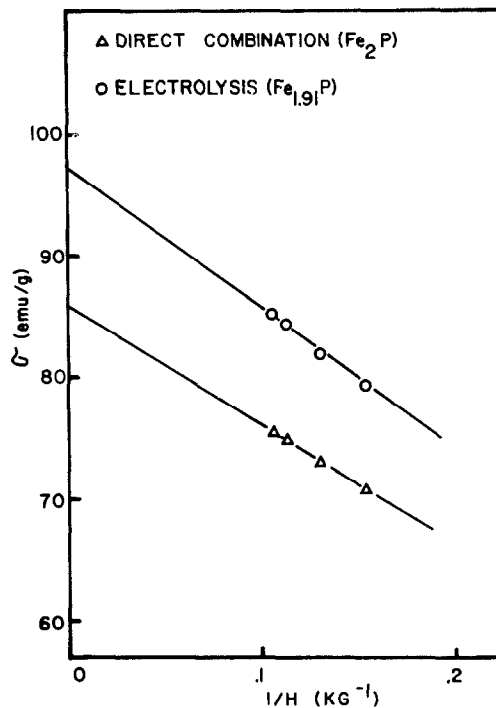


FIG. 4. Determination of maximum magnetization for Fe₂P and Fe_{1.91}P at 4.2°K.

observations of Meyer and Cadeville are also given in Table IV. It is interesting to note that the numerical values are quite similar, but the compositions are reversed. However, since Meyer and Cadeville did not report any chemical analysis with their results,

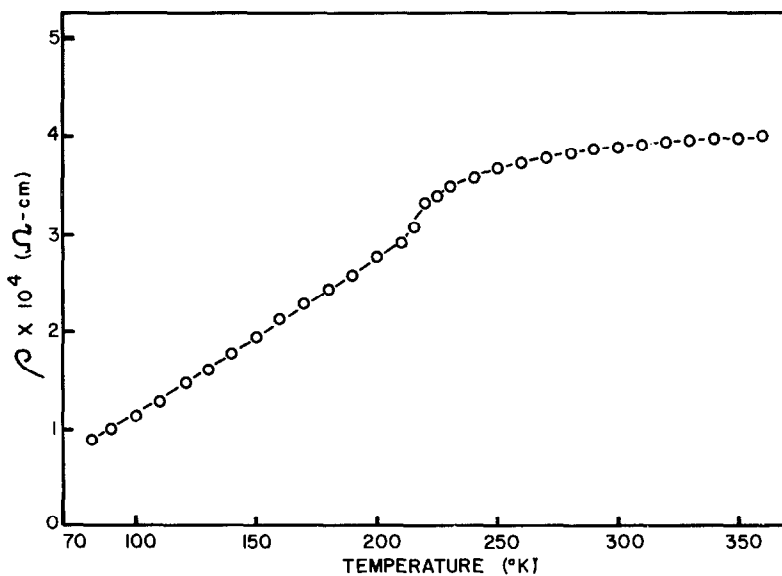


FIG. 5. Resistivity versus temperature for single crystals of Fe_{1.91}P.

TABLE IV
OBSERVED MAGNETIC MOMENT PER IRON ATOM
IN μ_B IN STOICHIOMETRIC AND NONSTOICHIOMETRIC Fe_2P

	Fe_2P	$Fe_{2-\delta}P$
This study	1.10	1.28
Meyer and Cadeville (4, 5)	1.32	1.07

there is some doubt in their assignment of stoichiometries.

The results of this study indicate that the stoichiometric material has the lower moment. A possible explanation, consistent with the experimental observations, is similar to that used by Stoner (15) to account for the variation in the moment as a function of composition in transition metal alloys. It is proposed that there is a saturated spin-up band and a partially filled spin-down band in stoichiometric Fe_2P . As iron atoms are removed from the structure, presumably in a manner similar to the removal of metal atoms in Co_2P (11), Mn_2P (10), and Ni_2P (10), less electrons are available to populate the higher energy spin-down band, and, since the spin-up band remains saturated, the net moment increases.

Four-probe resistivity measurements were carried out on single crystals of $Fe_{1.91}P$ prepared by electrolysis. The results of these measurements are shown in Fig. 5. $Fe_{1.91}P$ exhibits metallic behavior throughout the region 80–360°K. An abrupt change

in the resistivity was observed for all samples at about 220°K. This is in agreement with the magnetic behavior and Curie point of 223°K for $Fe_{1.91}P$.

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