

Magnetic and Crystallographic Properties of the System $\text{Fe}_2\text{P}_{1-x}\text{As}_x$ *

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The crystallographic and magnetic properties of the system $\text{Fe}_2\text{P}_{1-x}\text{As}_x$ were studied between $0 < x < 0.65$. The end member Fe_2P was prepared by both direct combination of the elements and electrolysis of fused salts. The products obtained showed similar crystallographic properties and were found to be stoichiometric. Differences in the magnetic properties were attributed to carbide impurities present in the samples prepared by electrolysis. The substitution of arsenic takes place preferentially on the anion_I site. The cell volume was found to increase monotonically with arsenic substitution, and the observed magnetic properties were interpreted on the basis of the Stoner model for itinerant electrons.

Introduction

The series of dimetallic transition metal phosphides M_2P ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) have been the subject of several recent investigations [1-3]. Many of these compounds are of interest because they form solid solutions which have interesting magnetic properties [1, 4-7]. Rundqvist [8] has characterized non-stoichiometric samples in the range of $\text{Co}_{1.94}\text{P}$ and found that they crystallize in the orthorhombic (C-23) system. Several recent investigators [1, 9, 10, 11] have also studied the properties of the system Fe_{2-x}P (hexagonal C-22) but their results are not in agreement.

The structure of diiron phosphide was first reported by Hendricks and Kosting [12] and later refined by Rundqvist and Jelinek [5]. The structure is illustrated in Fig. 1 projected on the basal plane. Two crystallographically different sites exist, Fe_I sites lying at $z = 0$ are tetrahedrally coordinated by phosphorus atoms, whereas Fe_{II} atoms lying at $z = 1/2$ are located at the base of a square pyramid. Fe_{II} atoms form a net enclosing prisms formed by Fe_I . Two non-equivalent phosphorus sites are located at the centers of metal atom tetrakaidehedra. The P_I ($z = 0$) tetrakaidehedra are linked in the basal plane to three other P_I tetrakaidehedra. Thus an infinite network of six-membered rings is formed.

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P_{II} ($z = 1/2$) atoms are located within the tetrakaidecahedral voids created by this network. Phosphorus atoms coordinating tetrahedral-site iron are in the ratio $\text{P}_I:\text{P}_{II} = 1:1$ whereas around the square-base-pyramid site, $\text{P}_I:\text{P}_{II} = 4:1$. Iron sites are present in equal numbers, whereas phosphorus sites occur in the ratio $\text{P}_I:\text{P}_{II} = 2:1$.

Rundqvist [8] has shown, by means of X-ray and chemical studies of Co_2P single crystals, that there is a well defined stoichiometry range in the system Co_{2-y}P . A similar range of homogeneity was also found for Mn_2P and Ni_2P , which crystallize in the Fe_2P -type structure [13]. Haughton [9], investigating uncharacterized material belonging to the Fe-P phase diagram

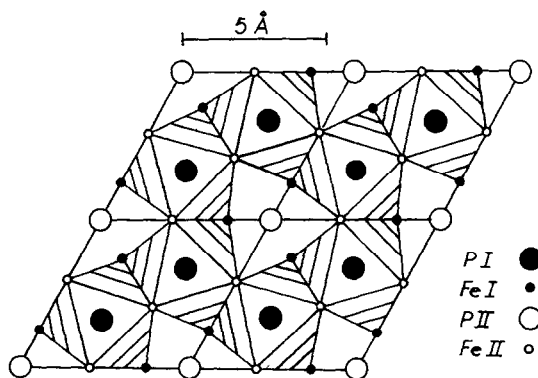


FIG. 1. Fe_2P structure projected on basal plane.

TABLE I

REPORTED VALUES OF MAGNETIC MOMENT FOR Fe_{2-x}P

	Meyer and Cadeville [10]	Fruchart [1]	Bellavance [11]
Fe_2P	1.38 μ_{β}/Fe	1.34 μ_{β}/Fe	1.10 μ_{β}/Fe
Fe_{2-x}P	1.07 μ_{β}/Fe	1.22 μ_{β}/Fe	1.28 μ_{β}/Fe

reported a range of homogeneity at high temperature. Meyer and Cadeville [10], and Fruchart [1] have reported the magnetic properties of non-stoichiometric diiron phosphide. These data as well as those recently reported by Bellavance [11] are given in Table I. Bellavance [11] has reported the synthesis of crystals of $\text{Fe}_{1.91}\text{P}$ by electrolysis of a fused salt mixture. The composition of the product was established by chemical analysis. No changes in cell dimensions were reported for the non-stoichiometric composition.

Fruchart *et al.* [1] have studied the magnetic properties and Mossbauer spectra of compositions of the solid solutions $\text{MM}'\text{P}$ ($\text{MM}' = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$). They have demonstrated the influence of cation-cation interaction on the structure type as well as the magnetic properties of the solid solutions. Their investigations of the systems $\text{Mn}_x\text{Fe}_{1-x}\text{P}$ and $\text{Mn}_x\text{Co}_{1-x}\text{P}$ have established the sensitivity of magnetic properties to electron concentration in the neighborhood of compositions isoelectronic with Fe_2P . Mössbauer spectroscopy revealed cation ordering in these solid solutions, with the smaller cation preferring generally the tetrahedral site. Wappling *et al.* [3] have established that cation ordering in some solid solutions is dependent on the thermal history of the sample.

More recently, Nylund *et al.* [2] have studied the role of arsenic substitution in the system $\text{MnCoP}_{1-x}\text{As}_x$. It was established that magnetic properties of this phase (isoelectronic with $\text{Fe}_2\text{P}_{1-x}\text{As}_x$) were influenced indirectly by anion substitution (MnCoP , $T_c = 583$ K, $\mu = 1.52$ μ_{β}/Fe ; MnCoAs , $T_c = 350$ K, $\mu = 1.58$ μ_{β}/Fe). This occurred because the $\text{M}-\text{M}'$ distances were modified by anion substitution. No study of preferred anion site ordering was made. This study is concerned with establishing the physical properties of the end member Fe_2P , as well as characterizing the non-stoichiometric phase reported by Bellavance [11]. Furthermore, the role of anion substitution is investigated in the system $\text{Fe}_2\text{As}_x\text{P}_{1-x}$ ($0 \leq x \leq 0.65$)

Part I. The System Fe_{2-x}P

Experimental

 Fe_{2-x}P preparation

The non-stoichiometric phase Fe_{2-x}P ($x \sim 0.09$) was synthesized according to the method of Bellavance [11]. A fused salt mixture of iron(III) fluoride and sodium metaphosphate was electrolyzed in a graphite crucible that also acted as an anode. A graphite rod was inserted as the cathode. The apparatus was flushed continuously with argon in order to prevent oxidation. The electrolysis was accomplished by melting a mixture of the starting materials ($\text{Fe}/\text{P} = 0.60$) at 900°C and passing a current of 400 mA, through the melt. Iron(III) fluoride was obtained from Ozark-Mahoning Co. (95%) and also from the action of 40% hydrofluoric acid on spectroscopically pure iron(III) nitrate. Crystals obtained by this method were removed from the melt by the action of dilute (1:6) hydrochloric acid. Carbon particles were removed from the product by flotation with methylene iodide.

Sample Characterization

The powder X ray diffraction pattern of all samples was obtained on polycrystalline samples using a Norelco diffractometer and a high intensity copper source ($\lambda K\alpha_1 = 1.54051$ Å). A graphite-crystal, reflected-beam monochromator was also employed. All reflections were indexed on the Fe_2P -type structure.

Unit cell dimensions were obtained from the least squares refinement of high-angle ($140^\circ \geq 2\theta \geq 75^\circ$) reflections. Magnesium oxide was used as an internal standard. These values are reported in Table II. The densities of all samples were

TABLE II

UNIT CELL DIMENSIONS FOR $\text{Fe}_2\text{As}_x\text{P}_{1-x}$

Composition x	a -Cell edge ± 0.0015 Å	c -Cell edge ± 0.001 Å	Cell volume
0.0	5.868	3.456	103.08
0.1	5.928	3.438	104.59
0.2	5.976	3.425	105.92
0.3	6.020	3.418	107.27
0.4	6.057	3.415	108.50
0.5	6.094	3.414	109.80
0.6	6.125	3.418	111.01
0.65	6.138	3.423	111.68

TABLE III

	Observed density (g/cc)	Calculated density (g/cc)
Fe ₂ P (direct comb.)	6.90	6.89
Fe ₂ P (electrolysis)	7.12–6.94	6.64 (Fe _{1.91} P)
Fe ₂ As _{0.3} P _{0.7}	7.26	7.24
Fe ₂ As _{0.6} P _{0.4}	7.56	7.58

determined by the displacement method using perfluoro(1-methyldecalin). Polycrystalline samples were used for density measurements. Calculated and experimental values are given in Table III.

All samples prepared were analyzed spectroscopically. The products obtained from 95% iron(III) fluoride contained 200–1000 ppm nickel, 50–250 ppm cobalt, and 400–800 ppm carbon. A sample of the material prepared from spectroscopically pure iron contained only trace amounts of transition metal impurities, but carbon was still present.

Magnetic Measurements

Magnetization of all samples was studied from 4.2 K to the Curie point using a vibrating sample magnetometer (Princeton Applied research, Model FM-1) that could alternatively be fitted with a variable temperature cryostat or with a furnace for measurements above room temperature.

Curie temperatures were calculated from high-field, isothermal magnetization data according to the method of Kouvel and Fisher [15].

Magnetic susceptibility was measured by the Faraday method using the experimental arrangement devised by Morris and Wold [16]. Susceptibility was measured to a maximum temperature of 650 K.

Ferromagnetic impurities were studied by the method of Honda and Owens [17]. Non-magnetic samples possessing ferromagnetically ordered impurity phases give non-zero slopes for plots of isothermal susceptibility data versus inverse field.

Calculations of effective paramagnetic moment were based on the familiar Curie-Weiss law assuming spin-only contributions.

Results and Discussion

The density of Fe_{1.91}P, prepared by electrolysis from fused salts, is expected to be lower (6.64g/cc)

than that of Fe_{2.00}P (6.89g/cc), prepared by direct combination of the elements. As shown in Table III the measured densities for diiron phosphide samples prepared by electrolysis (ranging between 6.94 and 7.15g/cc) are much closer to that expected for the stoichiometric phase Fe₂P than for Fe_{1.91}P. In addition, the unit cell dimensions for all compounds prepared are similar, and hence there is little evidence in this work for the existence of a non-stoichiometric phase. Recently, Rundqvist [18] has observed that a stoichiometry range does exist for the system Fe_{2-x}P. However, it was necessary to prepare samples by quenching from temperatures above 900°C. Unit cell dimensions of these materials were found to vary with changes in composition.

The problem, nonetheless, remains to explain the observed ferromagnetic moment of 1.28μ_B/Fe (4.2 K) for the phase obtained by electrolysis as compared to the value 1.11μ_B/Fe for stoichiometric Fe₂P reported by Bellavance and this study. Although transition metal impurities were eliminated by the use of pure starting materials, the electrolytic method of preparation introduces carbon contamination from the graphite electrode and crucible.

The paramagnetic behavior of the electrolytically prepared phase is consistent with the presence of carbide impurities. Honda-Owens plots (Fig. 2) indicate a gradual disappearance of a ferromagnetic impurity by 525 K. The observed value of the Curie temperatures for the ferromagnetic phases Fe₂C and Fe₃C are 485 K and 520 K, respectively [19]. It may therefore be concluded that iron carbide impurities appear

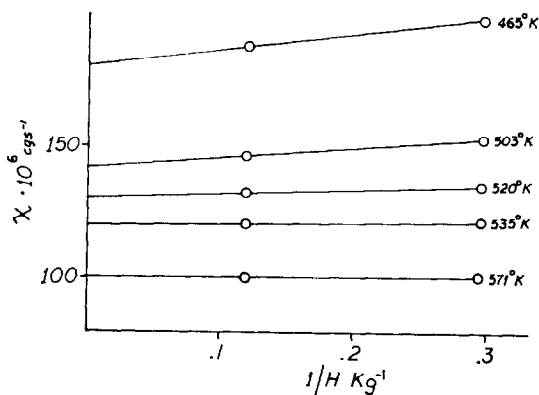


FIG. 2. Honda-Owens plot for Fe₂P prepared by electrolysis.

responsible for the higher magnetic moment of the samples prepared by electrolysis. The higher values reported by other investigators (Table I) for the magnetic moments of Fe_2P samples, prepared by direct combination of the elements, are also probably caused by the presence of carbide impurities.

Part II. The System $\text{Fe}_2\text{P}_{1-x}\text{As}_x$

Sample Preparation

Members of the series $\text{Fe}_2\text{P}_{1-x}\text{As}_x$ were prepared by direct combination of the elements. Spectroscopic grade iron was reduced prior to use by heating it to 950°C for 20 hr in a gas stream composed of 15% hydrogen, 85% argon. Arsenic (III) oxide was removed from elemental arsenic by heating the material in vacuo to 200°C , and phosphorus was used without further treatment. Stoichiometric amounts of the elements were sealed under vacuum in silica tubes and reacted at 900°C for five days, then cooled at a rate of $5^\circ/\text{hr}$ to room temperature. Two additional five day heat treatments were generally necessary to prepare a single phase material. All compositions were subjected to an additional fifteen days treatment at 900°C to insure homogeneity.

Sample Characterization

The density of selected compositions were measured by the method previously described for Fe_{2-x}P . These results are compared with the calculated values of density in Table III.

X-ray powder diffraction patterns of all compositions were obtained by the experimental arrangement previously described. All compositions for $x = 0.65$ exhibited the Fe_2P -type structure. Compositions prepared in the range $0.85 \geq x \geq 0.65$ yielded mixtures of the Fe_2P and Fe_2As -type (tetragonal) phases. Above $x = 0.85$ the tetragonal phase appears stable.

Magnetic Measurements

Measurements of magnetic susceptibility and magnetization were made in the range of 4.2 K to 650 K using the experimental arrangement described in Part I for Fe_{2-x}P .

Crystallography

Unit cell dimensions for the series of solid solutions $\text{Fe}_2\text{As}_x\text{P}_{1-x}$, where $0 \leq x \leq 0.65$, were determined from the least squares refinement of high angle X-ray diffraction data as previously described for Fe_{2-x}P . These results are summar-

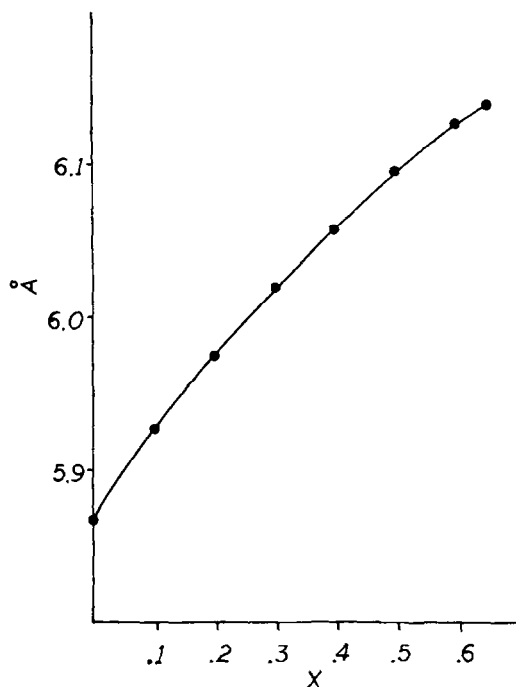


FIG. 3. "a" cell edge dimension as a function of composition x for $\text{Fe}_2\text{As}_x\text{P}_{1-x}$.

ized in Table II and illustrated graphically in Figs. 3 and 4.

As shown in Table IV, the only variable atomic parameters for the Fe_2P structure are the two values x_1 and x_{11} for the two iron positions. These parameters were determined from intensity data collected for the first twenty-three lines of the two samples $\text{Fe}_2\text{As}_{0.1}\text{P}_{0.9}$ and $\text{Fe}_2\text{As}_{0.3}\text{P}_{0.7}$. Data were collected by repeated scanning over

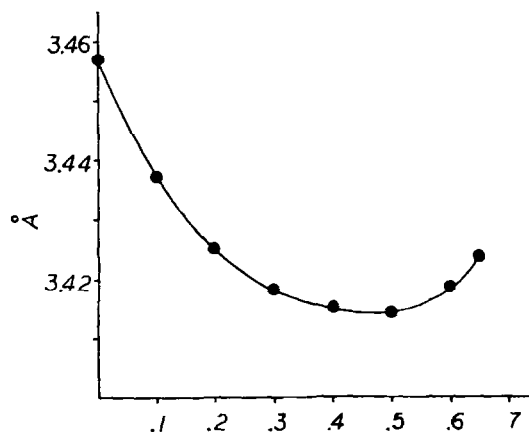


FIG. 4. "c" cell edge dimension as a function of composition x for $\text{Fe}_2\text{As}_x\text{P}_{1-x}$.

TABLE IV

ATOMIC POSITIONS FOR ATOMS IN THE Fe_2P -TYPE (C-22) UNIT CELL DUE TO RUNDQVIST AND JELLINEK [5]

Space Group: $\overline{\text{P6}}2\text{M}-(\text{D}_3^2)$
3FeI in 3(f): $x_100; 0x_10; \bar{x}_1\bar{x}_10$
3FeII in 3(g): $x_{11}0\ 1/2; 0x_{11}\ 1/2; \bar{x}_{11}\bar{x}_{11}\ 1/2$
2PI in 2(c): $1/3, 2/3, 0; 2/3, 1/3, 0$
PII in 1(b): $00\ 1/2$

each peak and subtraction of the background measured. Refinement of the variable atomic position parameters and cell temperature factor was made using a computer program that used the Simplex method to minimize the function,

$$R = 100 \sum_i |I_i^{\text{calcd}} - I_i^{\text{obsd}}| / \sum_i I_i^{\text{obsd}}$$

The atomic scattering factors for Fe^{2+} , P and As were those of Cromer and Waber [20] while the real and imaginary parts of the anomalous dispersion correction were those of Cromer [21]. For both samples two trials were made, one assuming a random distribution of anions and the other assigning arsenic to the I sites only. In the case of each composition, the R factor was somewhat lower with anion ordering. The parameters determined are given in Table V and compared with those of Rundqvist and Jellinek [5] for Fe_2P .

The possibility of anion ordering suggested by this result was investigated further. The relative intensities for the (00 l) reflections allow a method of distinguishing between three different cases possible: arsenic ordering on the I site, arsenic ordering on the II site, and the random distribution of arsenic over both sites. The structure factor for the (00 l) reflection is:

$$F_{00l} = 3f_{\text{FeI}} + 3f_{\text{FeII}} e^{2\pi i l/2} + 2f_{\text{P}_1} + f_{\text{P}_{11}} e^{2\pi i l/2} \quad (1)$$

For odd values of l , expression (1) becomes

$$F_{00l} = 2f_{\text{P}_1} - f_{\text{P}_{11}} \quad (2)$$

while for even values of l , this reduces to

$$F_{00l} = 6f_{\text{Fe}} + 3f_{\text{P}} \quad (3)$$

Therefore the ratio of the intensities of odd and even lines is dependent upon the distribution of anions over the two sites.

The intensity ratio I_{001}/I_{002} was calculated for each of the anion distributions and these results

TABLE V

RESULTS OF THE DETERMINATION OF IRON POSITION PARAMETERS x_I AND x_{II} AS WELL AS THOSE DUE TO RUNDQVIST AND JELLINEK [5]

	Fe_2P [5]	$\text{Fe}_2\text{As}_{0.1}\text{P}_{0.9}$	$\text{Fe}_2\text{As}_{0.3}\text{P}_{0.7}$
x_I	0.256	0.255	0.256
x_{II}	0.594	0.594	0.590

are shown in Fig. 5 along with the observed values of I_{001}/I_{002} . Intensity data was collected by the method previously described. Useful intensity data could only be obtained for samples with $x = 0, 0.4, 0.5$ and 0.6 . For all other samples the (002) reflection was overlapped by the (300) reflection.

Results and Discussion

Table II shows an increase in the observed cell volume as arsenic is substituted for phosphorus. This is expected due to the larger size of the arsenic atom. Changes in the a -cell edge distance also reflect this trend. The behavior of the c -edge distance is anomalous, since it decreases with initial substitution, but reaches a minimum at about $x = 0.5$.

Iron position parameters x_I and x_{II} appear to be little influenced by arsenic substitution (Table V).

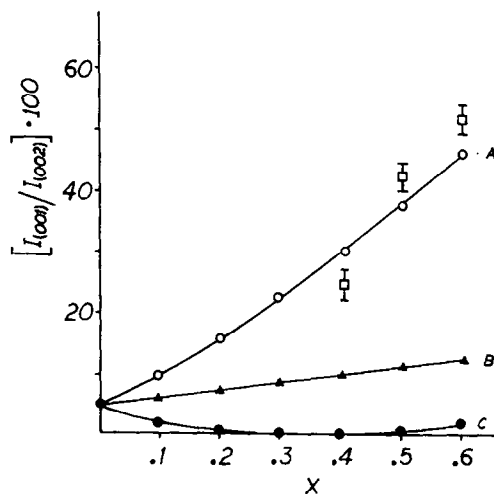


FIG. 5. Calculated intensity ratios for three cases of arsenic substitution. (a) arsenic ordered on anion I site, (b) arsenic randomly distributed over both I and II sites, (c) arsenic ordered on anion II sites. (Squares represent experimentally observed intensities. Bars indicate experimental error).

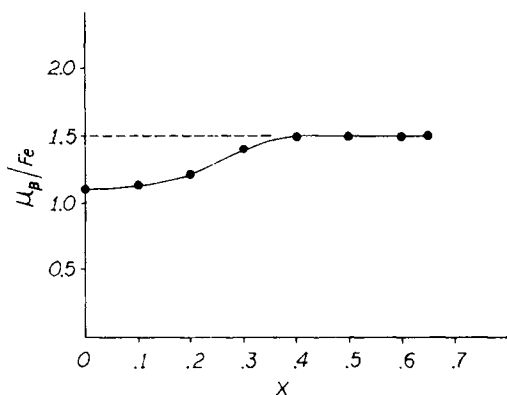


FIG. 6. Observed ferromagnetic moment (4.2 K) for compositions $\text{Fe}_2\text{As}_x\text{P}_{1-x}$.

Small arsenic substitutions thus do not alter the relative atomic positions within the unit cell.

Arsenic ordering on the P_I site has been shown to exist for compositions $x \geq 0.4$ from intensity measurement. Results also suggest that this ordering extends to lower arsenic substitution as well. It is worthwhile to note that the anion I site becomes completely filled with arsenic atoms at the composition $x = 0.666$. Based on these two facts it is concluded that the Fe_2P structure type is stabilized by ordering of arsenic on I sites and that this stability is removed when arsenic can no longer assume this position. All samples in the range $0.0 \leq x \leq 0.65$ exhibited ferromagnetic behavior. Fig. 6 illustrates the behavior of the saturation moment as a function of composition. Although initial arsenic substitution does not result in a significant change in moment, a rapid increase can be seen to occur in the neighborhood

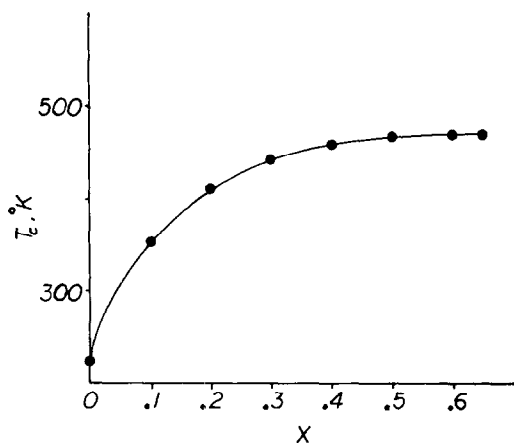


FIG. 7. Curie temperature as a function of composition x , $\text{Fe}_2\text{As}_x\text{P}_{1-x}$.

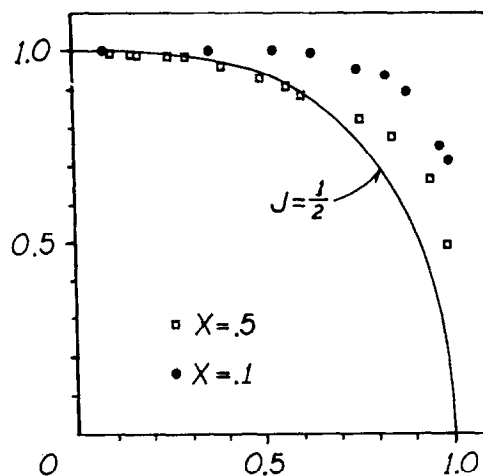


FIG. 8. Reduced magnetization vs reduced temperature for $x = 0.1, 0.5$ as well as the Brillouin function for $J = \frac{1}{2}$.

of $x = 0.3$. Further arsenic addition results in a maximum value of $1.50\mu_B/\text{Fe}$ for all compositions having $x \geq 0.4$. Paramagnetic data summarized in Table VI shows a similar increase in spin only moment for $0.2 \leq x \leq 0.4$ and leveling off at higher concentrations.

The Curie temperature is plotted as a function of arsenic substitution in Fig. 7. A 133 K increase in Curie point results from 10 atomic percent substitution for phosphorus in Fe_2P . Above $x = 0.4$, the Curie temperature reached a constant value of 470 K. A similar behavior is noted for the Weiss constant in Table VI.

The increase in intermetallic distance that results from arsenic substitution would be expected to decrease the orbital overlap between adjacent atoms, resulting in a decrease in bandwidth. Martin [22] has shown that in the limit of extremely narrow bands, the Stoner (delocalized) model approaches the Weiss model for $J = \frac{1}{2}$. The Brillouin function (Fig. 8) for $J = \frac{1}{2}$ is plotted with reduced magnetization M/M_s versus reduced temperature for the compositions $\text{Fe}_2\text{As}_{0.1}\text{P}_{0.9}$ and $\text{Fe}_2\text{As}_{0.5}\text{P}_{0.5}$. It can be seen that a significantly better fit to $J = \frac{1}{2}$ behavior is given by the higher arsenic substitution. It therefore appears that the result of arsenic substitution in Fe_2P is to cause an increase in the localized nature of magnetic electrons through the mechanism of increased interatomic distances. The limiting value of $1.50\mu_B/\text{Fe}$ found for the ferromagnetic moment appears due to the details of the band structure of the material. This matter will be taken up in another paper.

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