PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

## Magnetic Properties of Iron-Phosphorus Compounds\*

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Fe<sub>3</sub>P, Fe<sub>2</sub>P, FeP, FeP<sub>2</sub> have been prepared and their magnetic properties investigated. Fe<sub>3</sub>P, Fe<sub>2</sub>P and FeP are ferromagnetic with respective Curie points at 716, 266 and 215°K, and absolute moments of 1.84, 1.32 and 0.36 Bohr magnetons per iron atom in the molecules. Fe<sub>(2-e)</sub>P is much more difficult to saturate than Fe<sub>2</sub>P, but has otherwise the same magnetic properties. In spite of very high anisotropy energies due to the low crystalline symmetries, the coercive fields of the three compounds are limited. FeP<sub>2</sub> seems to be antiferromagnetic.

The phase diagram of Fe and P, shows that whereas at room temperature the solubility of P in  $\alpha$ -Fe does not exceed 0.026 at.%, there exist several stable definite compounds: Fe<sub>3</sub>P, Fe<sub>2</sub>P, FeP, FeP<sub>2</sub> which are respectively tetragonal, hexagonal, orthorhombic and orthorhombic<sup>1)</sup>. The first two of these compounds have in the past been recognized as ferromagnetics, but no other data than their Curie temperature have been established until now<sup>2), 8)</sup>. However, in view of the low crystalline symmetry of the compounds, the study of their ferromagnetic properties should be interesting. We prepared and studied the 4 compounds and found that Fe<sub>3</sub>P, Fe<sub>2</sub>P and FeP are ferromagnetic, whereas FeP<sub>2</sub> is paramagnetic with negative Curie points.

 $Fe_3P^{4}$  has been prepared by high frequency furnace melting of a compressed powder mixture of Fe and P weighed with Fe excess, giving a mixture of Fe<sub>3</sub>P and  $\alpha$  Fe-P solution which is dissolved out by cold nitric Fe<sub>3</sub>P remains as small tetragonal acid. shaped needles, which are easily melted without phosphorus loss, the liquid compound showing a high stability. Fe<sub>2</sub>P<sup>5)</sup> has been prepared, following Maronneau's method<sup>6)</sup>, by melting a compressed powder mixture of 1Fe, 1P, 9Cu parts in weight. Hot nitric acid dissolves all compounds of the resulting mixture except Fe<sub>2</sub>P which remains as small hexagonal shaped needles which are easily melted, showing like Fe<sub>3</sub>P a high thermal stability. Prolonged melting at high temperature removes a small quantity of P (0.2% by weight) probably dissolved in the lattice of  $Fe_2P$ . Thus we studied  $Fe_2P$  and  $Fe_{(2-\epsilon)}P$ . FeP has been prepared by H<sub>2</sub> reduction of FePO<sub>4</sub> at 800°C<sup>7)</sup>. The obtained gray powder can no more be melted without an appreciable phosphorus loss. FeP<sub>2</sub> was obtained by heating in sealed quartz tubes a stoichiometric powder mixture of Fe<sub>3</sub>P and P at 1000°C for two hours<sup>8)</sup> giving a fine homogeneous powder which cannot be separated by magnetic sorting. FeP and FeP<sub>2</sub> have been studied in powder form, whereas Fe<sub>3</sub>P and Fe<sub>2</sub>P were studied in bulk and powder form.

We studied the ferromagnetic and paramagnetic properties of the compounds. The most important data are given in comparative form in Table I.

Fe<sub>3</sub>P. This ferromagnetic tetragonal compound has its Curie point  $\theta_f$  at 443°C in agreement with previous observagood tions<sup>2),3)</sup>. Thermomagnetic analysis shows the usual ferromagnetic behaviour (Fig. 1). The approach to saturation which obeys a law  $\sigma_{H,T} = \sigma_{\infty,T}(1-b/H_i^2)$  is very slow, indicating that the compound is magnetically very hard. At room temperature  $b=6.07\times10^6$ ,  $\sigma_{\infty} = 143.8 \text{ e.m.u./gm.}$  and  $I_{\infty} = 143.8 \times 7.13 =$ 1025 e.m.u./cm<sup>3</sup>. Saturation magnetization is  $\sigma_{\infty,0^{\circ}K} = 155.4 \text{ e.m.u./gm.}$  leading to a saturation moment M of 1.84  $\mu_{Bohr}$  for one iron atom in the molecule. The small tetragonal Fe<sub>3</sub>P needles, when placed in a homogeneous field orient themselves with their axes normal to the field, showing that the magnetization vector lies in the basal plane of the tetragonal unit cell. The anisotropy energy has been measured on oriented grains: if simply expressed as  $K_1 \sin^2 \theta + K_2 \sin^4 \theta$ , one gets  $K_1 = -5.3 \times 10^6$  and  $K_2 = 2.4 \times 10^6$  ergs/cm<sup>3</sup>. The coercive field measured on a fixed powder is 107 Oe at room temperature, which indicates a low anisotropy energy in the basal

This paper was not read at the Conference.

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18	Fe <sub>3</sub> P	Fe <sub>2</sub> P	$\mathrm{Fe}_{(2-\mathfrak{g})}\mathrm{P}$	FeP	FeP <sub>2</sub> T>300°K	FeP <sub>2</sub> T < 230°K
θ <sub>f</sub> ,°K	716	266	266	215	A	
<i>σ</i> ∞,0° K	155.4	103.4	e-Weise, Indifful	23.6	Eabo	
(e.m.u./gm)			tobourg, France.	NIS.		
$M(\mu_B/Fe)$	1.84	1.32	opared and their	0.36	Fell, Fell, Felle	Re.P.
θ <sub>p</sub> °K	781	443	437	335	-17 646 9	-56
См	4.23	1.95	1.93	0.496	0.249	0.416
$P_{(\mu_B/Fe)}$	1.94	1.97	1.96	2.00	1.41	1.82













plane of the unit cell. The paramagnetic behaviour above the Curie point is the usual Curie-Weiss law  $C = (T - \theta)\chi$ . Paramagnetic Curie point  $\theta_p$ , molecular Curie constant  $C_M$ and conventional paramagnetic moment Pare given in Table I.

Fe<sub>2</sub>P. This ferromagnetic hexagonal compound has its Curie point at  $-7^{\circ}$ C. Thermomagnetic analysis shows a different behaviour for  $Fe_2P$  and  $Fe_{(2-\varepsilon)}P$ . (Figs. 2, 3, 4). The stoichiometric Fe<sub>2</sub>P sample shows the usual parabolic decrease of the magnetization with increasing temperature. The coefficient b of the law of approach  $\sigma_{H,T} = \sigma_{\infty,T}(1-b/H_i^2)$  is, as for Fe<sub>3</sub>P, very high. At 20°K,  $b=1.73\times10^7$ leading to  $K_1 = 2.74 \ b^{1/2} I_{\infty} = 8.2 \times 10^6 \ \text{ergs/cm}^3$ if the anisotropy energy is limited to its first term  $E_a = K_1 \sin^2 \theta$  and if one neglects tension energies. The magnetization vector lies along the hexagonal axis since the hexagonal Fe<sub>2</sub>P needles orient themselves parallel to a homogeneous field. Saturation mag-



netization is  $\sigma_{\infty,0^{\circ}K}=103.4 \text{ e.m.u./gm}$  and  $I_{\infty,0^{\circ}K}=103.4\times6.85=708 \text{ e.m.u./cm}^3$  leading to a saturation moment of 1.32  $\mu_{\text{Bohr}}$  for one iron atom in the molecule. The coercive



1000 %

500

Fig. 7.

250

01

field is about 450 Oe at 108°K whereas  $H_c = 2K_1/I_s \simeq 2.3 \times 10^4$  Oe. The  $\sigma = f(T)$  curves of the non-stoichiometric  $\operatorname{Fe}_{(2-e)} P$  sample are unusual as they remain flat over an extended temperature range. The increase of the magnetization in high fields is very slow. As there is a spontaneous magnetization it seems that this behaviour is due to an extreme magnetic hardness of the samples. However, the coercive field is only 220 Oe at 77°K after magnetization in 24000 Oe. Both Fe<sub>2</sub>P and Fe<sub>(2-e)</sub>P have the usual paramagnetic behaviour above their Curie points with essentially the same constants (Table I).

FeP. This ferromagnetic orthorhombic compound has its Curie point at 215°K (Figs. 5 and 6). Magnetization measurements give  $\sigma_{\infty,0^{\circ}K}=23.6$  e.m.u./gm or a saturation moment of 0.36  $\mu_{Bohr}$  for the molecule. The field increase of  $\sigma$  is again very slow: at 20°K the rotation coefficient of the law of approach is  $b=6.9\times10^7$  leading with the same approximations as for Fe<sub>2</sub>P to  $K_1\simeq3.3\times10^6$  ergs/cm<sup>3</sup>. The high temperature paramagnetic behaviour is again usual (Table I).

FeP<sub>2</sub>. This orthorhombic compound is paramagnetic in the investigated temperature range from 77 to 900°K. The  $1/\chi = f(T)$ graph (Fig. 7) shows an anomaly in the vicinity of 250°K. Above and below this temperature  $1/\chi$  varies linearly as a function of *T*, extrapolating to paramagnetic Curie points at  $-17^{\circ}$ K and  $-56^{\circ}$ K (Table I): thus FeP<sub>2</sub> seems to be antiferromagnetic.

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