Structural and Magnetic Properties of FeP

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Some 25 years elapsed from Fylking[1] determined the crystal structure of FeP (MnP type) until the systematic examination of its physical and chemical properties was continued. However, from about 1960 onwards there has been a considerable amount of effort devoted to the study of FeP by modern experimental techniques such as nuclear magnetic resonance,[2,3] Mössbauer spectroscopy,[3-6] and neutron diffraction[7] in addition to the more classical methods X-ray diffraction,[8,9] electrical resistivity,[10] magnetization,[11] and magnetic susceptibility.[2,10-14] Despite these efforts the properties of FeP are not understood in detail, and, in fact, three simple questions readily emerge on considering the literature data:

(i) Has FeP an appreciable range of homogeneity? This problem has not hitherto been subjected to a systematic investigation.

(ii) Is $Pna2_1$ or $Pnma$ (b and c interchanged) the appropriate space group for description of the crystal structure of FeP? This question is relevant in view of the findings for the (formally) isostructural compounds FeAs[15] and CoAs.[16]

(iii) The temperature dependence of the magnetic susceptibility of FeP below (say) room temperature appears to be well established through the work of Bellavance *et al.*[10] Of what kind is the characteristic at higher temperatures?

The sole purpose of the present paper is to answer these questions.

Experimental. The samples were prepared from 99.99+ % Fe (Johnson, Matthey & Co.; turnings from rods) and 99.999 % red P (Koch-Light Laboratories) by heating weighed quantities of the components in evacuated and sealed silica tubes at 550°C for 10 days. After careful grinding the samples were reannealed at 550°C for another 10 days and finally cooled to room temperature over a period of 3 days.

Single crystals were prepared by chemical transport reactions, using iodine (~ 1 mg/ml capsule volume) as the transport agent. A good yield of suitable crystals was obtained (after 7 days) by applying a temperature gradient ~ 1.5°C/mm along a ~ 200 mm long (evacuated and sealed) silica capsule, with the hot end containing powdered FeP at 850°C.

X-Ray diffraction (Weissenberg and Guinier photographs), density, magnetic susceptibility, and diffuse reflectance measurements, as well as the computational work, were performed as described previously.[16]

Results. The composition of the FeP phase, which has no appreciable range of homogeneity, was determined by the disappearing phase principle applied to Guinier photographs of samples with different nominal compositions. The room temperature unit cell dimensions $a = 5.193(1)$ Å, $b = 5.792(1)$ Å, $c = 3.099(1)$ Å (setting according to space group $Pna2_1$), as determined from Guinier photographs, were found to be constant within experimental error for the different samples. These values are in excellent agreement with those reported by Refs. 6 − 8, 10. The formula FeP was also confirmed by comparison of the pycnometrically measured density ($d_{\text{pycn.}} = 6.13$ g cm^{-3}) with that calculated from the unit cell dimensions and a cell content of 4 FeP-groups ($Z_c = 3.96$).

The MnP type structure of FeP has been confirmed in several independent studies,[1,7-9] and its essential features are clearly correct. Analogous refinement models to those tried for FeAs[15] and CoAs[16] were considered, including the possibility of anisotropic as well as isotropic temperature factors. Least squares refinements of the structure factor data were continued until no shifts were obtained in all variables of each model. Using the Hamilton[17] test in judgements between the different models it was found that the model specified by the following parameters: $x = 0.0020(4)$, $y = 0.2004(3)$, $z = 1/4$ (fixed), $B = 0.07(2)$ Å^2 for Fe in $4(a)$ and $x = 0.1912(7)$, $y = 0.5684(6)$, $z = 0.296(5)$, $B = 0.04(3)$ Å^2 for P in $4(a)$ according to space group $Pna2_1$ is superior to all the others at a significance level < 0.005. The present values for the positional parameters x and y for both kinds of atom are in excellent agreement with those reported by Rundqvist and Nawapong.[9] However, in contrast with their findings our results show that there is no mirror plane perpendicular to [001] at $z = 1/4$ (and $z = 3/4$) in the crystal structure of FeP (as evidenced by the significant deviation of z_P from 1/4).

The present values for the unit cell dimensions and positional parameters lead to the following interatomic distances: 2.186(11), 2.247(5), 2.258(11), 2.351(4),
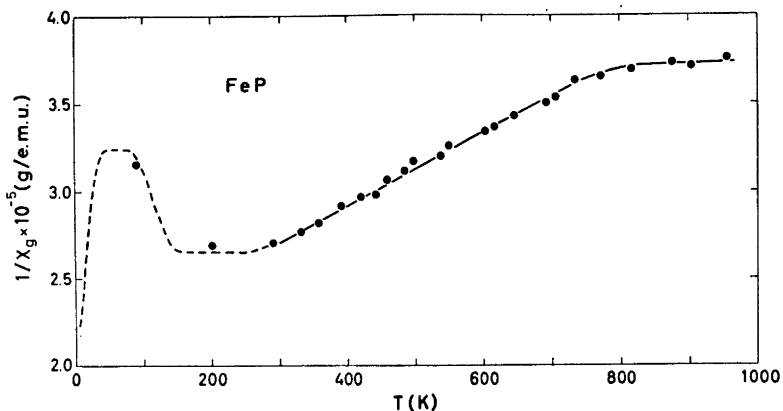
Fig. 1. Reciprocal magnetic susceptibility *versus* temperature for FeP. The broken portion of the curve is quoted from Bellavance *et al.*[10]

2.380(12), and 2.447(12) Å (average 2.312 Å) for the bonding Fe – P distances and 2.658(3), 2.791(2), and 2.640(14) Å for the possible bonding distances of the types Fe – Fe, Fe – Fe, and P – P, respectively.

The diffuse reflectance of FeP decreases uniformly from 2 400 to 20 000 Å, with no observed absorption edge or other anomalies. This is consistent with the metallic type of electrical conduction observed by Bellavance *et al.*[10]

The temperature dependence of the reciprocal magnetic susceptibility is shown in Fig. 1, good reproducibility being obtained between a number of different samples of FeP crystals. Field strength dependent susceptibilities were not observed and the experimental points represent mean values at different field strengths without correction for induced diamagnetism.

The Curie-Weiss Law, $\chi^{-1} = C^{-1}(T - \theta)$, is satisfied over the interval $300 - 750$ K with $\theta = -1000 \pm 50$ K and $\mu_P = \sqrt{8C_{\mathrm{mol}}} = 1.83 \pm 0.05$ B.M./Fe atom. The equivalent spin quantum number according to the "spin only" approximation ($\mu = g\sqrt{S(S+1)}$ with $g = 2$) is $S = 0.54 \pm 0.02$. The present values for θ and μ_P are substantially different from those reported by Chiba.[12] Below 300 K the $\chi^{-1}(T)$-curve shows a positive deviation from the Curie-Weiss Law relationship, and as demonstrated in Fig. 1 our results concur with those of Bellavance *et al.*[10]

A more comprehensive discussion of these and similar results for the isostructural compounds will be presented in a forthcoming paper.

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