

## CONCENTRATION DEPENDENCE OF THE MAGNETIC PROPERTIES IN AMORPHOUS Fe-P-B ALLOYS

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## ABSTRACT

The concentration dependence of the magnetic properties of amorphous Fe-P-B alloys obtained by splat-cooling is discussed. For a given Fe concentration, the magnetic moment  $\bar{\mu}$  averaged over all atoms of material and the Curie temperature  $T_c$  both increase with the substitution of B for P. We observed for the variation of  $\bar{\mu}$  and  $T_c$  as a function of the B content the same discontinuity as that occurring between the two phases  $\epsilon$  and  $\epsilon_1$  of the crystalline  $\text{Fe}_3\text{P}_{1-x}\text{B}_x$  compounds. We studied also the variation of  $\bar{\mu}$  and  $T_c$  when one metalloid (P or B) substitutes for Fe, the other metalloid remaining constant.  $\bar{\mu}$  was found to decrease when the P (or B) content is increased, as expected from a rigid band model. For the same concentrations,  $T_c$  increases. The different behaviours of  $\bar{\mu}$  and  $T_c$  are tentatively explained by assuming that the amorphous Fe has two magnetic states (ferro and antiferromagnetic) as already suggested for crystalline Fe in a fcc environment.

## INTRODUCTION

The relationship between the magnetic properties of splat-cooled amorphous Fe alloys and the metalloid concentrations has received little attention so far. It is commonly admitted that the metalloid s-p electrons contribute to fill up the Fe d-bands according to the rigid band model, which results in a lowering of the magnetic moment.<sup>1</sup> On the other hand, Chen<sup>2</sup> pointed out an increase of  $T_c$  in amorphous Fe-P-C alloys when the concentration of one metalloid is increased, the other one remaining constant. So it seemed interesting to undertake a thorough investigation of the metalloid content dependence of the magnetic properties in the Fe-P-B amorphous alloys. This system is particularly suitable for such a study. First, the amorphous phase is available over a relatively broad concentration range; in particular, one can obtain a quasi-complete substitution of B for P at a given Fe concentration (75-83 at. %). Second, a comparison is possible with the crystalline  $\text{Fe}_3\text{P}_{1-x}\text{B}_x$  compounds, whose crystal structures<sup>3</sup> and magnetic properties<sup>4</sup> were studied to some extent in recent years. We measured  $T_c$  and  $\bar{\mu}$  at 4.2°K, and electrical resistivity as a function of the temperature as well<sup>13</sup>, on Fe-P-B samples over all the concentration range available in the amorphous structure.

## EXPERIMENTAL PROCEDURES

The samples were quenched from the melt by the "piston and anvil technique".<sup>5</sup> Full details of the alloy preparation may be found elsewhere.<sup>6</sup> Each foil was checked with a Norelco X-ray diffractometer. Concentrations are nominal.

$T_c$  was measured by an inductance bridge.<sup>7</sup> The sample is at the center of an induction coil. Variation of the magnetic permeability is recorded when the temperature goes through the Curie transition. The apparatus was calibrated with high-purity Ni. The Curie transition was found to be constant and extremely sharp (from 1 to 3°K) for all the samples we studied, in complete contrast with the electro-deposited Fe-P amorphous alloys, where the Curie transition measured with the same apparatus was found to be rather broad (from 10 to 50°K, depending on the P content).<sup>8</sup>  $T_c$  was found to be the same

( $\pm 0.5^\circ\text{K}$ ) for different parts of a given foil. Scattering between different foils of the same nominal concentration does not exceed 3°K, even when one of these foils exhibits some traces of crystallization. After annealing, the Curie transition is sharper and occurs at 2 or 3°K higher than in as-quenched samples. The values of  $T_c$  reported below for each concentration are an average taken from three foils after annealing,  $T_c$  being defined as the inflexion point of the transition.

Saturation magnetization was measured by the Faraday method with an Oxford Instruments Magnetometer.<sup>9</sup> Three discs of about 5 mg were taken from edge parts of the foils. Central parts of the foils do not exhibit a good reproducibility. Measurements were performed up to 30 kOe, in order to avoid any demagnetizing field effect. Actually a complete saturation is reached between 5 and 10 kOe, as for the Fe-P-C amorphous alloys.<sup>10</sup> The apparatus was calibrated with foils of pure Fe. The values of  $\bar{\mu}$  listed in this paper are the average taken from edge parts of two foils of the same nominal concentration. The uncertainty is estimated to  $\pm 0.5\%$ .

## RESULTS AND DISCUSSION

## 1. Substitution of B for P at Fe constant. Two different short-range orders in amorphous Fe-P-B.

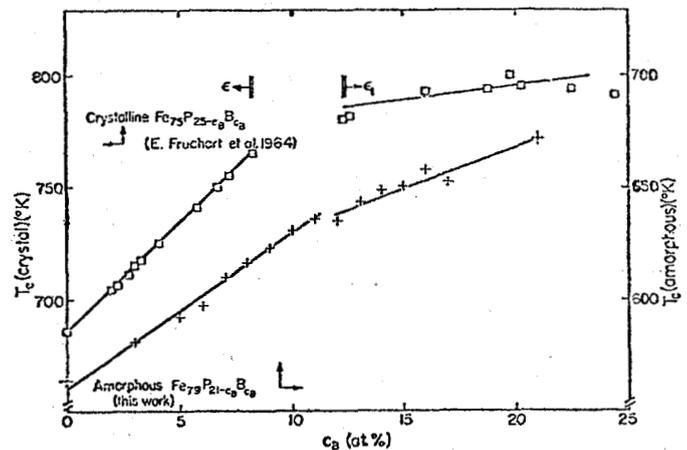


Fig. 1. Variation of the Curie temperature  $T_c$  with the B content  $c_B$  in amorphous  $\text{Fe}_{79}\text{P}_{21-c_B}\text{B}_{c_B}$  (+) and in crystalline  $\text{Fe}_{75}\text{P}_{25-c_B}\text{B}_{c_B}$  (ref. 4) (□).

The values of  $T_c$  (fig. 1) and  $\bar{\mu}$  (fig. 2) are plotted as a function of  $c_B$ . Alloys were found to be amorphous for  $3 \leq c_B \leq 17$  at. %. We plotted also in dash the values obtained for  $\text{Fe}_{79}\text{P}_{21}$  and  $\text{Fe}_{79}\text{B}_{21}$ , although these splat-cooled alloys exhibited traces of crystallinity.

For  $c_B \leq 11$  at. %,  $T_c$  increases at a rate of 7°K/at. %; for  $c_B > 11$  at. %, the slope is about 5°K/at. %. For  $c_B \leq 14$  at. %,  $d\bar{\mu}/dc_B = 0.92\mu_B/\text{at.}$  For  $c > 14$  at. %,  $\bar{\mu}$  is roughly constant. These features will be explained by comparison with the crystal structures and the magnetic properties of the crystalline  $\text{Fe}_{75}\text{P}_{25-c_B}\text{B}_{c_B}$  compounds.

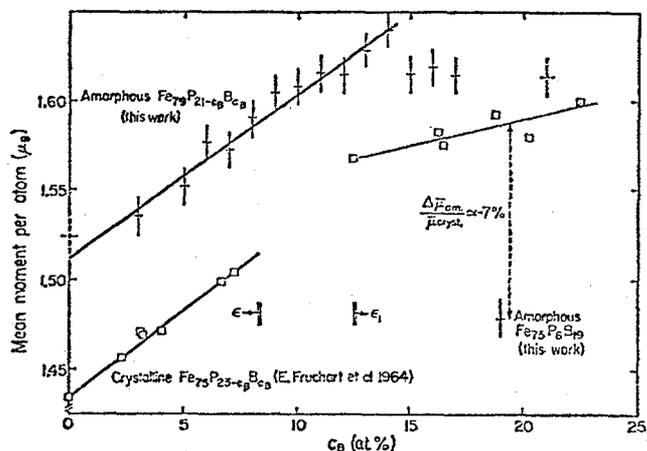


Fig. 2. Variation of the mean magnetic moment per atom  $\bar{\mu}$  at 4.2°K with the B content  $c_B$  in amorphous  $\text{Fe}_{79}\text{P}_{21-c_B}\text{B}_{c_B}$  (+) and in crystalline  $\text{Fe}_{75}\text{P}_{25-c_B}\text{B}_{c_B}$  (ref. 4)(□).

Structural and magnetic properties of crystalline  $\text{Fe}_{75}\text{P}_{25-c_B}\text{B}_{c_B}$

B substitutes for P to a large extent in  $\text{Fe}_3\text{P}$ .<sup>3</sup> Up to  $c_B = 8.2$  at.%, the crystal structure of  $\epsilon$ - $\text{Fe}_3\text{P}$  is preserved (tetragonal of the  $\text{Ni}_3\text{P}$  type). For  $8.2 < c_B < 12.3$  at.%, there is a gap of solubility. For  $12.3 \leq c_B \leq 24.4$  at.%, the compound crystallizes in a new ternary phase called  $\epsilon_1$ - $\text{Fe}_3\text{P}_{1-x}\text{B}_x$  (tetragonal also, but not isomorphous to  $\text{Ni}_3\text{P}$ ).  $\text{Fe}_3\text{B}$  does not exist.

The variation of the magnetic properties<sup>4</sup> (results are collected on fig. 1 and 2) is different in the  $\epsilon$  and  $\epsilon_1$  phases: in the  $\epsilon$  phase,  $dT_c/dc_B = 9.5^\circ\text{K/at.}\%$  and  $d\bar{\mu}/dc_B = 0.97 \mu_B/\text{at.}\%$ ; in the  $\epsilon_1$  phase, the variation of  $T_c$  and  $\bar{\mu}$  is definitely smoother than in the  $\epsilon$  phase, but the slopes are not very well defined. The increase of the magnetic properties as a function of  $c_B$  may be roughly accounted for by a rigid band model. But this model fails to explain the experimental value for  $d\bar{\mu}/dc_B$  even in the  $\epsilon$  phase ( $1\mu_B$  instead of  $2\mu_B$ , as expected from the difference of s-p electrons number in P and B). The different behaviours of  $T_c$  and  $\bar{\mu}$  in the two phases were explained by a contraction of the  $\text{Fe}_{\text{III}}-\text{Fe}_{\text{III}}$  distances in the  $\epsilon_1$  phase.<sup>4</sup>

Comparison between amorphous and crystalline Fe-P-B.

As shown in fig. 1 and 2, the change of slope for  $T_c$  occurs at about  $c_B = 12$  at.% in both crystalline and amorphous alloys. In the amorphous Fe-P-B,  $\bar{\mu}$  seems to increase with the same slope up to  $c_B = 14$  at.%. In the crystalline case, the values of  $\bar{\mu}$  for the compounds at the "beginning" of the  $\epsilon_1$ -phase ( $c_B = 12.5$  at.%) are also in the trend of the straight line defined for  $\bar{\mu}(c_B)$  in the  $\epsilon$ -phase. So, the change of slope seems to occur for  $T_c$  at a smaller value of  $c_B$  than for  $\bar{\mu}$  in both crystalline and amorphous Fe-P-B. This discrepancy may be due to the fact that  $T_c$  is more sensitive than  $\bar{\mu}$  to the changes in the crystal structure or in the short-range order (SRO).

It is well established that in the amorphous alloys of transition metals M with metalloids m ( $\text{M}_{80}\text{m}_{20}$  type) the coordination numbers CN for M and m are the same as in the crystalline counterpart ( $\text{M}_3\text{m}$  compounds, typically).<sup>11</sup> Our study suggests that two different SRO in the amorphous Fe-P-B correspond to

the two phases in the  $\text{Fe}_3\text{P}_{1-x}\text{B}_x$  compounds. These two SRO would not differ by the CN (which are the same in both  $\epsilon$  and  $\epsilon_1$  phases), but only by the mean interatomic distances.

The effect of the long-range disorder in amorphous Fe-P-B may explain that the change of slope for  $T_c$  is less drastic between the  $\epsilon$  and  $\epsilon_1$  SRO regions than between the  $\epsilon$  and  $\epsilon_1$  phases in the compounds. However, the values of  $d\bar{\mu}/dc_B$  are approximately the same in the  $\epsilon$ -SRO region and in the  $\epsilon$ -phase. The influence of the lack of long-range order in the  $\epsilon_1$ -SRO region may be evaluated by comparing the values of  $T_c$  (694 and 794°K, respectively) and  $\bar{\mu}$  (1.48 and 1.59  $\mu_B$  per atom) for the amorphous and crystalline  $\text{Fe}_{75}\text{P}_6\text{B}_{19}$  (fig. 2). The values in the amorphous alloy are lowered by 7% for  $\bar{\mu}$  and by 12% for  $T_c$ , which is the same order of magnitude as for the lowering of the local field at Co nuclei in amorphous Co as determined from NMR measurements.<sup>12</sup>

2. Substitution of one metalloid for iron, the content of the other metalloid being kept constant.

Experimental results. From a rigid band picture one would expect a decrease of both  $T_c$  and  $\bar{\mu}$  when P or B substitutes for Fe,  $c_B$  ( $c_P$ , respectively) remaining constant. In fact,  $T_c$  and  $\bar{\mu}$  were found to vary as a function of  $c_B$  ( $c_P$ ) in an opposite way. We present two examples for some alloys in the  $\epsilon$ -SRO region ( $c_B < 12$  at.%):  $\text{Fe}_{87-c_B}\text{P}_{13}\text{B}_{c_B}$  (fig. 3) and

$\text{Fe}_{92-c_P}\text{P}_{c_P}\text{B}_8$  (fig. 4). We observed the same

behaviour for all the sets of  $c_P$  and  $c_B$  values we investigated.

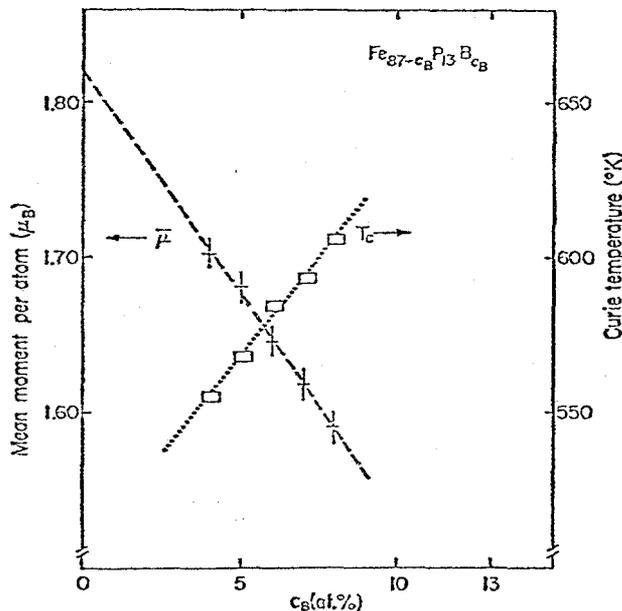


Fig. 3. Variation of the mean magnetic moment per atom  $\bar{\mu}$  at 4.2°K (+) and the Curie temperature  $T_c$  (□) as a function of  $c_B$  in amorphous  $\text{Fe}_{87-c_B}\text{P}_{13}\text{B}_{c_B}$ .

Extrapolations. From fig. 3 and 4, one can obtain the extrapolated values of  $T_c$  and  $\bar{\mu}$  for  $\text{Fe}_{87}\text{P}_{13}$  and  $\text{Fe}_{92}\text{B}_8$ . From the different sets of concentrations in the Fe-P-B system, we were able to define by similar extrapolations the variation of  $T_c$  and  $\bar{\mu}$  in the  $\text{Fe}_{100-c_P}\text{P}_{c_P}$  ( $4 \leq c_P \leq 23$  at.%) and in the  $\text{Fe}_{100-c_B}\text{B}_{c_B}$  ( $4 \leq c_B \leq 13$  at.%) amorphous alloys. For the Fe-B alloys, the extrapolated values are in

good agreement with the results obtained on binary Fe-B alloys obtained by splat-cooling<sup>13</sup> ( $17 \leq c_B \leq 21$  at.%). For the Fe-P alloys, a comparison with the values measured on electrodeposited Fe-P alloys is not significant, the magnetic properties of these latter alloys exhibiting a very particular behaviour as a function of  $c_P$ .<sup>8, 13</sup> From our study of the Fe-P-B alloys, the moment of "pure" amorphous Fe extrapolates to about  $2.3 \mu_B$ , and its Curie temperature is less than  $300^\circ\text{K}$ . This low value for  $T_c$  agrees fairly well with the values ( $T_c = 200$  and  $270^\circ\text{K}$ ) obtained independently from studies on R.E.-Fe amorphous alloys.<sup>14</sup>

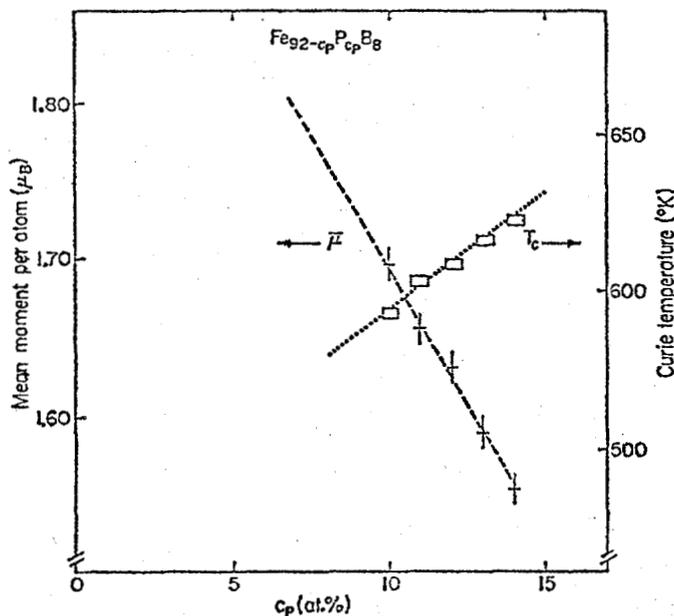


Fig. 4. Variation of the mean magnetic moment per atom  $\bar{\mu}$  at  $4.2\text{ K}$  (+) and of the Curie temperature  $T_c$  ( $\square$ ) as a function of  $c_P$  in amorphous  $\text{Fe}_{92-c_P}\text{P}_{c_P}\text{B}_8$ .

**Discussion.** Our value of  $T_c$  for "pure" amorphous Fe indicates only a trend. Our extrapolation is done from  $c_B(c_P) \geq 4$  at.%. On the other hand, a small amount of oxygen may be easily trapped in our samples. So, the real value for  $T_c$  of pure amorphous Fe is likely to be considerably lower. For the same reasons, the value we propose for  $\bar{\mu}$  of amorphous Fe has to be suspected. Measurements performed on amorphous films of Fe-Si, Fe-O, showed<sup>15</sup> that the moment of Fe drops down drastically for very low concentrations of impurities.

So, the magnetic properties of amorphous Fe seem to be very similar to those of fcc Fe, which are still controversial. The particular behaviour of  $\bar{\mu}$  and  $T_c$  as shown on fig. 3 and 4 may be tentatively explained as follows. The iron in a fcc (or compact) environment would have two magnetic states: Fe I, strongly ferromagnetic ( $\bar{\mu} = 2.3$  to  $3 \mu_B$ , high  $T_c$ ) and Fe II antiferromagnetic. Such a model was first proposed for the interpretation of the magnetic properties of fcc Ni-Fe alloys<sup>16</sup> and justified by recent calculations.<sup>17</sup> The low-value of  $T_c$  suggests that the population of Fe II states would be the majority in pure amorphous Fe. The number of Fe I states increases with the impurity concentration  $c$  at a rate depending on the nature of the impurity. When  $c$  reaches some critical value (different for Si, Ge, O)<sup>15</sup>, the Fe II states are polarized by the Fe I states, so

that all the Fe atoms seem to bear the same moment ( $2.3-3 \mu_B$ ) and, above this critical concentration, the variation of  $\bar{\mu}(c)$  agrees more or less with a rigid band model. Meanwhile,  $T_c$  remains proportional to the number of the Fe I states and increases monotonously. Unfortunately, the critical concentration for P and B is probably too small to be observed in amorphous Fe-P-B alloys.

## CONCLUSIONS

The variation of  $T_c$  and  $\bar{\mu}$  in amorphous Fe-P-B alloys when B substitutes for P presents the same singularities as in  $\text{Fe}_3\text{P}_{1-x}\text{B}_x$  compounds when the phase is changed, although the CN remains the same. It is suggested that, for the SRO in these amorphous alloys, not only the CN of the crystalline counterpart is preserved, but also the main structural properties of the corresponding crystal phase. The effect of long-range disorder was found to be of 7% for  $\bar{\mu}$  and 12% for  $T_c$  between an amorphous alloy and the compound of same composition in the  $\epsilon_1$ -SRO region. So the electronic structure of amorphous alloys of the  $M_{80}m_{20}$  type is likely to be very similar to that of compounds of the  $M_{3m}$  type.<sup>12</sup>

The variation of  $T_c$  and  $\bar{\mu}$  when P(B) substitutes for Fe, the content of the other metalloid remaining constant, suggests a strong similarity between amorphous Fe and crystalline Fe in a fcc environment. The model of the two magnetic states (ferro and antiferromagnetic) of fcc Fe yields some qualitative explanation for the concentration dependence of  $T_c$  and  $\bar{\mu}$  in amorphous Fe-P-B alloys.

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