CALT-822-83

RECEIVED
JUN 29 1976
CALIF. PATENT GR

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

J. Durand

MAY 1976

A REPORT ON RESEARCH CONDUCTED
UNDER CONTRACT FOR THE
U.S. ENERGY RESEARCH AND DEVELOPMENT
ADMINISTRATION

THERE IS NO OBJECTION FROM THE PATENT
STANDPOINT TO THE PUBLICATION OR
DISSEMINATION OF THIS DOCUMENT:
CALIFORNIA PATENT GROUP, ERDA
By:
Date: 7/2/76

W. M. KECK LABORATORY OF
ENGINEERING MATERIALS

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA

MASTER

CALT-822-83

California Institute of Technology
W. M. Keck Laboratory of Engineering Materials

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

by

J. Durand

Energy Research and Development Agency Report No. 73, under Contract No. AT(04-3)-822.

Professor Pol Duwez, principal investigator.

MAY 1976

NOTICE

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 per atom $\overline{\mu}$ and the Curie temperature T_c both increase with the substitution of B for P. We observed for the variation of $\overline{\mu}$ and T_c as a function of the B content the same discontinuity as that occurring between the two phases ε and ε_1 of the crystalline $Fe_3P_{1-x}B_x$ compounds. We studied also the variation of $\overline{\mu}$ and T_c when one metalloid (P or B) substitutes for Fe, the other metalloid remaining constant. The value of $\overline{\mu}$ was found to decrease when the P or B content is increased, as expected from a rigid band model. In the same concentration range, T_c increases with either P or B. The different behaviours of $\overline{\mu}$ 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 lowering the magnetic moment.[1] On the other hand, Chen[2] 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 $Fe_3P_{1-x}B_x$ compounds, whose crystal structures[3] and magnetic properties[4] were studied to some extent in recent years. We measured T_c and $\bar{\mu}$ at 4.2°K of 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".[5] Full details of the alloy preparation may be found elsewhere.[6] Each foil was checked with a Norelco X-ray diffractometer. Concentrations are nominal.

T_c was meausred by an inductance bridge.[7] 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 electrodeposited 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).[8] T_c was found to be the same (± 0.5°K) for different parts of a same foil. Scattering of results 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 transition.

Saturation magnetization was measured by Faraday method with an Oxford Instruments Magnetometer.[9] Three discs of about 5 mg were taken from the 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.[10] The apparatus was calibrated with foils of pure Fe. The values of $\overline{\mu}$ listed in this paper are the average taken from edge parts of two foils of the same nominal concentration. The uncertainty is estimated to ± 0.5%.

RESULTS AND DISCUSSION

A. Substitution of B for P at Fe constant. Two different short-range orders in amorphous Fe-P-B. Variation of $\overline{\mu}$ and T_c as a function of c_B in amorphous $Fe_{79}P_{21-c_B}B_{c_B}$.

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

For $c_B \le 11$ at.%, T_c increases at a rate of $7^{o}K$/at.%; for $c_B > 11$ at.%, the slope is about $5^{o}K$/at.%. For $c_B \le 14$ at.%, $d\overline{\mu}/dc_B = 0.92\mu_B$/at. For $c > 14$ at.%, $\overline{\mu}$ is roughly constant. These features will be explained by comparison with the crystal structures and the magnetic properties of the crystalline $Fe_{75}P_{25-c_B}B_{c_B}$ compounds.

Structural and magnetic properties of crystalline $Fe_{75}P_{25-c_B}B_{c_B}$.

B substitutes for P to a large extent in Fe_3P.[3] Up to $c_B = 8.2$ at.%, the crystal structure of ϵ - Fe_3P is preserved (tetragonal of the Ni_3P type). For $8.2 < c_B < 12.3$ at.%, there is a gap of solubility. For $12.3 \le c_B \le c_B \le 24.4$ at.%, the compound crystallizes in a new ternary phase called ϵ_1-$Fe_3P_{1-x}B_x$ (tetragonal also, but not isomorphous with Ni_3P). Fe_3B does not exist.

The variations of the magnetic properties[4] with concentration (fig. 1 and 2) are different for the ϵ and ϵ_1 phases: in the ϵ phase,

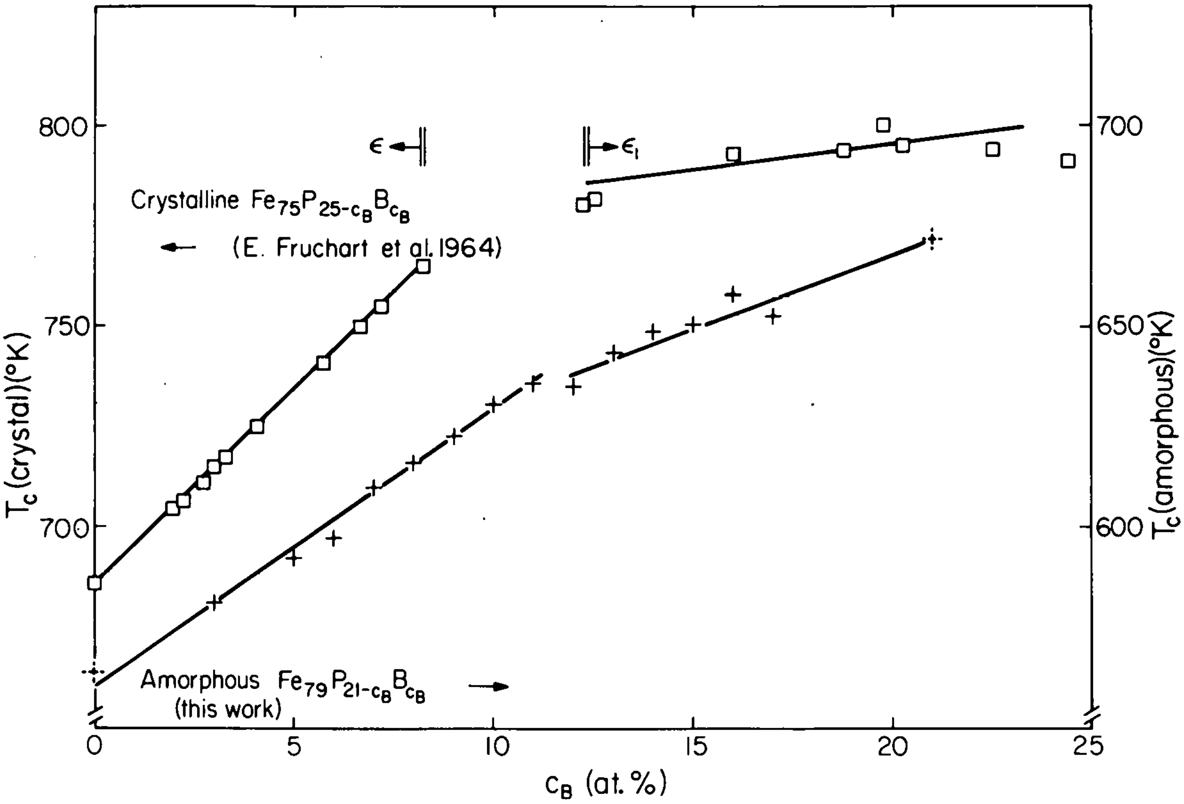

Fig. 1. Variation of the Curie temperature T_c as a function of the B content c_B in amorphous $Fe_{79}P_{21-c_B}B_{c_B}$ (+). The values of T_c in crystalline $Fe_{75}P_{25-c_B}B_{c_B}$ (ref. 4) are also shown (□).

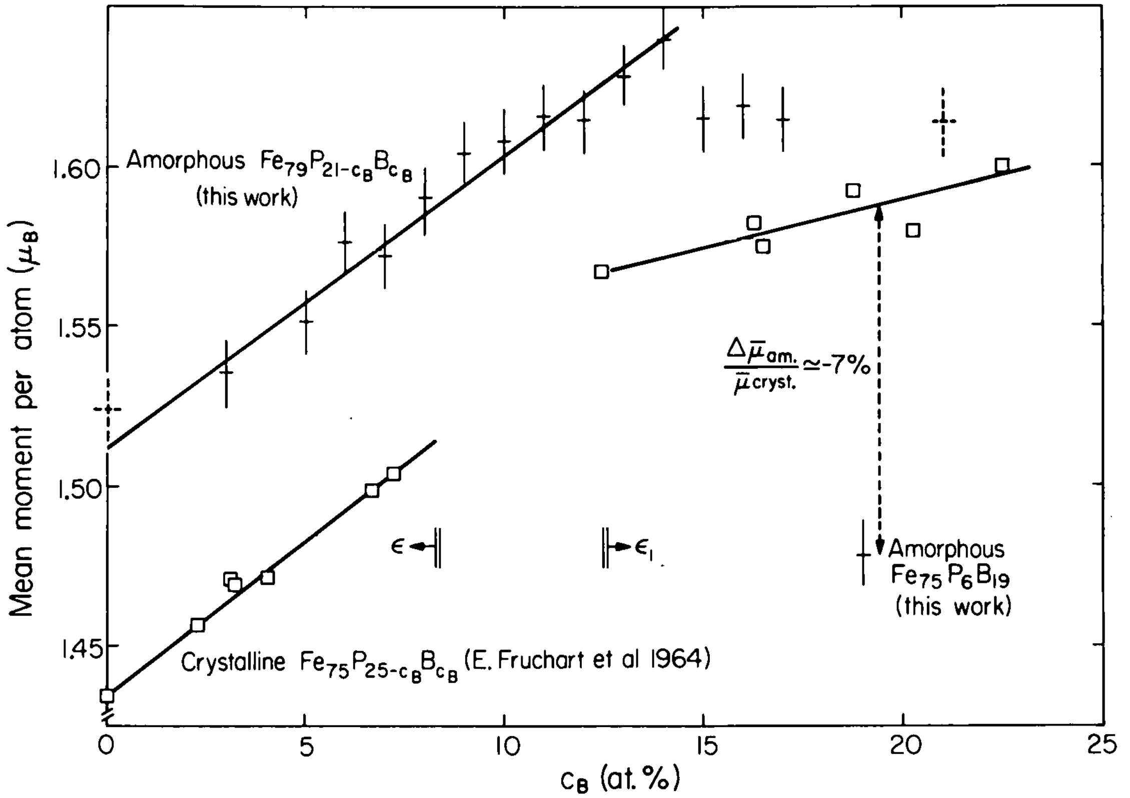

Fig. 2. Variation of the magnetic moment per atom $\bar{\mu}$ at 4.2°K as a function of the B content c_B in amorphous $Fe_{79}P_{21-c_B}B_{c_B}$ (+). The values of $\bar{\mu}$ in crystalline $Fe_{75}P_{25-c_B}B_{c_B}$ (ref. 4) are also shown (□).

$dT_c/dc_B = 9.5^{o}K/at.\%$ and $d\overline{\mu}/dc_B = 0.97\ \mu_B/at.$; in the ϵ_1 phase, the variation of T_c and $\overline{\mu}$ is definitely smoother than in the ϵ 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 $d\overline{\mu}/dc_B$ even in the ϵ 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 $\overline{\mu}$ in two phases were explained by a contraction of the Fe_{III}-Fe_{III} distances in the ϵ_1 phase.[4]

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, $\overline{\mu}$ seems to increase with the same slope up to $c_B = 14$ at.%. In the crystalline case, the values of $\overline{\mu}$ for the compounds at the "beginning" of the ϵ_1-phase ($c_B = 12.5$ at.%) are also in the trend of the straight line defined for $\overline{\mu}(c_B)$ in the ϵ-phase. So, the change of slope seems to occur for T_c at a smaller value of c_B than for $\overline{\mu}$ in both crystalline and amorphous Fe-P-B. This discrepancy may be due to the fact that T_c is more sensitive than $\overline{\mu}$ 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($M_{80}m_{20}$ type) the coordination numbers CN for M and m are the same as in the crystalline counterpart (M_3m compounds, typically).[11] Our study suggests that two different SRO in the amorphous Fe-P-B correspond to the two phases in the $Fe_3P_{1-x}B_x$ compounds.

These two SRO would not be affected by the CN which are the same in both ϵ and ϵ_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 ϵ and ϵ_1 SRO regions than between the ϵ and ϵ_1 phases in the compounds. However, the values of $d\bar{\mu}/dc_B$ are approximately the same in the ϵ-SRO region and in the ϵ-phase. The influence of the lack of long-range order in the ϵ_1-SRO region may be evaluated by comparing the values of T_c and $\bar{\mu}$ for the amorphous and crystalline $Fe_{75}P_6B_{19}$ (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.[12]

B. 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 ϵ-SRO region ($c_B < 12$ at.%): $Fe_{87-c_B}P_{13}B_{c_B}$ (fig. 3) and $Fe_{92-c_P}P_{c_P}B_8$ (fig. 4). We observed the same behaviour for all the sets of c_P and c_B values we investigated.

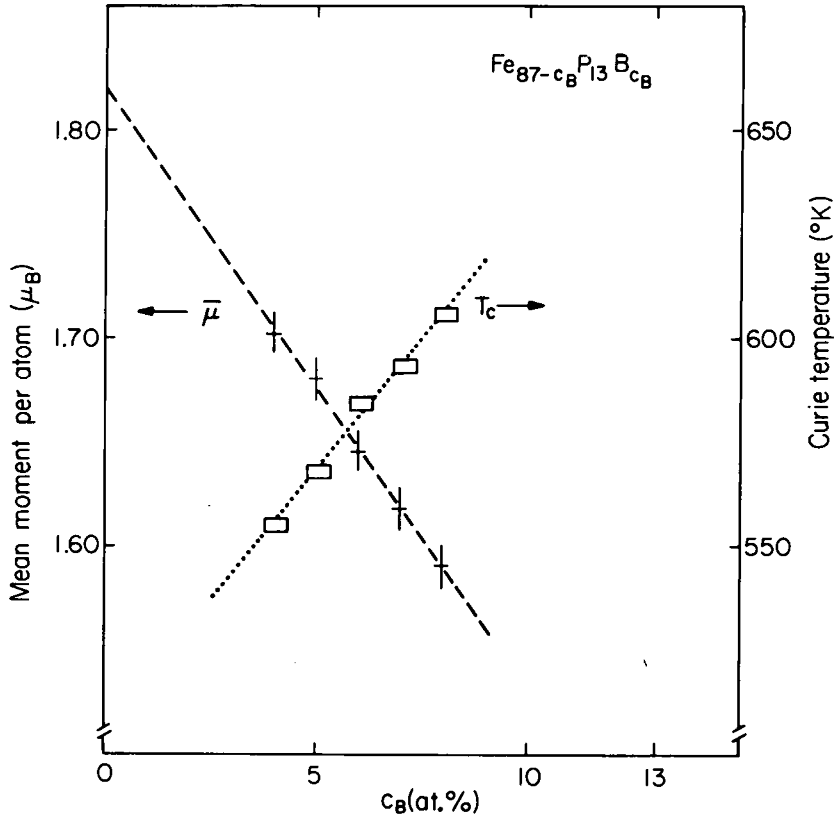

Fig. 3. Variation of the magnetic moment per atom $\bar{\mu}$ at 4.2°K (+) and the Curie temperature T_c (□) as a function of the B content c_B in amorphous $Fe_{87-c_B}P_{13}B_{c_B}$.

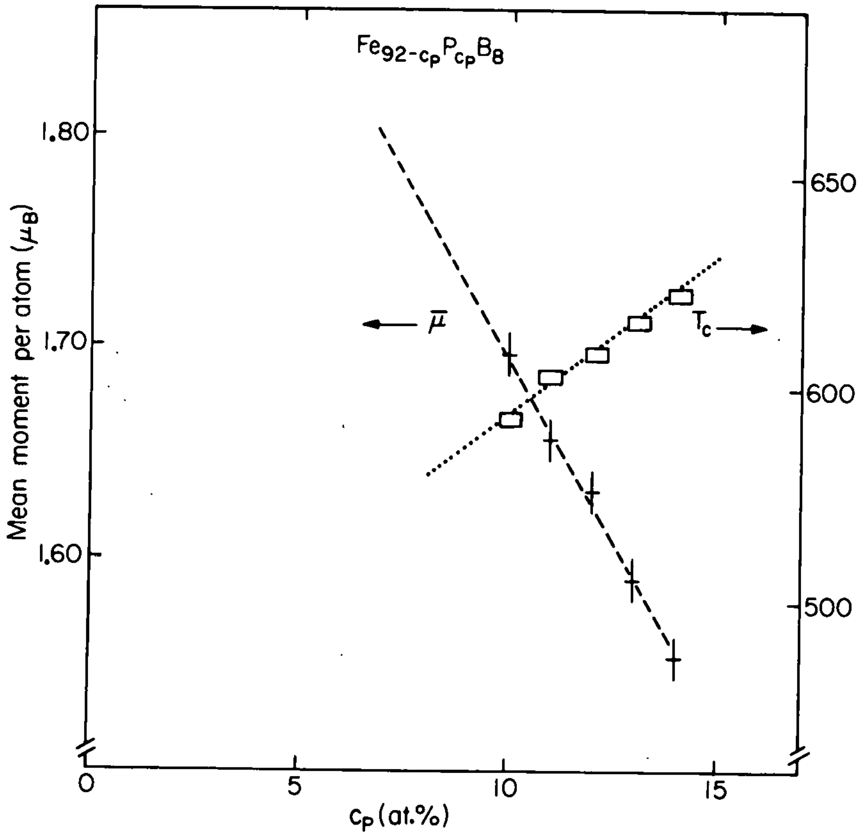

Fig. 4. Variation of the magnetic moment per atom $\bar{\mu}$ at 4.2°K (+) and of the Curie temperature T_c (□) as a function of the P content c_P in amorphous $Fe_{92-c_P}P_{c_P}B_8$.

Extrapolations.

From fig. 3 and 4, one can obtain the extrapolated values of T_c and $\bar{\mu}$ for $Fe_{87}P_{13}$ and $Fe_{92}B_8$. 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 $Fe_{100-c_P}P_{c_P}$ $(4 \leq c_P \leq 23$ at.%) and in the $Fe_{100-c_B}B_{c_B}$ $(4 \leq c_B \leq 13$ 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[13] $(17 \leq c_B \leq 21$ 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.[8, 13] 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°K. This low value for T_c agrees fairly well with the value (T_c = 240°K) obtained from studies on the $Fe_{100-x}Tb_x$ amorphous alloys $(x \geq 2$ at.%).[14]

Discussion.

Our value of T_c for "pure" amorphous Fe indicates only a trend. Our extrapolation is made 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[15] that the moment of Fe drops down drastically for very low concentrations of impurities. Hence, 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[16] and justified by recent calculations.[17] 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)[15], 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 to 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 $Fe_3P_{1-x}B_x$ 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 7% for $\bar{\mu}$ and 12% for T_c

between an amorphous alloy and the compound of same composition in the ϵ_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.[12]

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.

REFERENCES

1. K. Yamaushi and T. Mizoguchi, J. Phys. Soc. Japan 39, 541 (1975).
2. H. S. Chen, Phys. Stat. Sol. (a) 17, 561 (1973).
3. S. Rundqvist, Acta Chem. Scand. 16, 1 (1962).
4. E. Fruchart, A. M. Triquet and R. Fruchart, Ann. Chim. (Paris) 9, 323 (1964).
5. P. Duwez and R. Willens, Trans. AIME 227, 362 (1963).
6. P. L. Maitrepierre, J. Appl. Phys. 40, 4826 (1969).
7. S. C. H. Lin, Ph.D. Thesis, Caltech (1968).
8. J. Logan and E. Sun, J. Non-Cryst. Sol. 20, 285 (1976).
9. G. Tangonan, Ph.D. Thesis, Caltech (1975).
10. P. Duwez and S. C. Lin, J. Appl. Phys. 38, 4096 (1967).
11. J. Bletry and J. F. Sadoc, J. Phys. F 5, L110 (1975); J. F. Sadoc and J. Dixmier, Conf. Rapid-Quenched Mat. MIT 1975 (to be published).
12. J. Durand and M. F. Lapierre, J. Phys. F 6 (1976) (in press).
13. J. Durand, (to be published).
14. H. A. Alperin, J. R. Cullen and A. E. Clark, Conf. MMM, Philadelphia 1975 (to be published).

15. W. Felsch, Z. Physik 219, 280 (1969).

16. E. I. Kondorsky and V. L. Sedov, J. Appl. Phys. 31, 3315 (1960); R. J. Weiss, Proc. Phys. Soc. 82, 281 (1963); G. Blaise and M. C. Cadeville, J. Physique 36, 545 (1975).

17. T. Jo, J. Phys. Soc. Japan 40, 715 (1976).