

RADIATION EFFECTS IN  
AMORPHOUS METALLIC ALLOYS

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# ABSTRACT

During the first year changes in the Curie temperature and saturation magnetization of the first series above (with  $20 \leq x \leq 34$ ) induced by proton bombardment have been studied, and correlated with small angle x-ray scattering measurements performed for  $x = 20$  at Oak Ridge National Laboratory. Both the Curie temperature and the low temperature saturation magnetization increase with proton fluence up to  $10^{16} \text{ cm}^{-2}$  but are constant for higher fluences. By varying the proton energy it is concluded that hydrogen implantation is eliminated as the principal source of the observed changes. Proton bombardment at the same fluences produces scattering centers that are observed by small angle x-ray scattering. The size of the scattering centers is in the range of 16-30 Å.

Electron irradiation (1.25 MeV) produces an increase in Curie temperature similar to that following proton bombardment.

## I. Goals for The First Year: Progress to Date

In a letter of November 13, 1979, to Dr. John L. Warren, DOE, we outlined a schedule of goals for the first year. We review those goals and their implementation to date.

### 1. Complete Construction of Equipment for $T_c$ Measurements Above Room Temperature.

This equipment has been completed and put to use with a new lock-in amplifier. The equipment will operate in the  $T_c$  range from room temperature to approximately 400°C.  $T_c$  measurements on the  $Fe_{27}$  and  $Fe_{34}$  alloys reported in section 3 were made in this apparatus. This apparatus complements existing equipment that operates from liquid nitrogen to room temperature. Both the low and high temperature equipment can be evacuated and filled with helium, thereby avoiding the formation of an oxide layer during measurement.

### 2. Fabricate Ribbons of Varying Fe-Ni Composition and Characterize their Composition Using Proton Microprobe.

We have successfully made ribbons of  $Fe_{20}Ni_{60}P_{14}B_6$ ,  $Fe_{27}Ni_{53}P_{14}B_6$  and  $Fe_{34}Ni_{46}P_{14}B_6$ . Preliminary analysis on ribbon composition has been done using the proton microprobe. Results indicate a small loss (~1-2%) of phosphorous during ribbon fabrication but no macroscopic composition change induced by irradiation. These ribbons were made on our melt-spinner at Delaware.

### 3. Perform Series of Proton Irradiations at 2.5 MeV and 0.2 MeV.

Proton irradiations at 2.25 MeV and 0.25 MeV have been carried out on alloys of  $Fe_{20}$ ,  $Fe_{27}$ , and  $Fe_{34}$  composition. Since annealing can significantly alter the magnetic properties of amorphous alloys, care was exercised to control the sample temperature during irradiation so that measured changes are truly radiation caused changes. Ribbons of  $Fe_xNi_{80-x}P_{14}B_6$  prepared by single wheel spin quenching (thickness  $11 \pm 2 \mu m$ ) were wrapped continuously around a copper block of dimension

25 mm x 25 mm x 6 mm such that one 25 mm x 25 mm face was open to the proton beam during bombardment. The ribbons were subsequently cut from the block, leaving twenty 25 mm strips of ribbon from each 25 mm x 25 mm face. This technique enables the irradiation of every other inch of a ribbon, with the alternate 25 mm strips serving as virgin control samples which have had the same thermal history. This tends to minimize both thermal annealing effects on the measurements and trends in the data from gradual variations in composition along the length of the ribbon. To further minimize any annealing effects, beam currents were kept low (400 nA over 25 mm x 25 mm) so that the sample temperature never exceeded 40°C during irradiation, as measured by a thermocouple attached to the ribbon.

Samples of  $\text{Fe}_{20}\text{Ni}_{60}\text{P}_{14}\text{B}_6$  were bombarded with protons of energy 2.25 MeV (range greater than sample thickness) and 0.25 MeV (range less than sample thickness). Resultant changes in Curie temperature with proton fluence are shown in Fig. 1, indicating the difference in effect between bombardments of these two energies. Curie temperature measurements were made in a 60 Oe, 407 Hz ac field, rather than the customary vibrating sample in a dc field method. Measurements made by this technique agree quite well with those reported elsewhere.

The saturation magnetic moments of these samples were measured at 77°K and found to increase at a fractional rate of one-half the increase in Curie temperature. That is, a plot of  $\Delta M$  (sat) vs. fluence gives a function with the same shape as Fig. 1, reaching a maximum value at a fluence of about  $5 \times 10^{15} \text{ cm}^{-2}$ . The maximum fractional increase in  $\Delta M$  (sat) was 2%, while that for  $T_c$  was 4%.

Using the same technique, samples of  $\text{Fe}_{27}\text{Ni}_{53}\text{P}_{14}\text{B}_6$  and  $\text{Fe}_{34}\text{Ni}_{46}\text{P}_{14}\text{B}_6$  were bombarded with 2.25 MeV protons. The resultant changes in Curie temperature are shown in Fig. 2 along with the 2.25 MeV  $\text{Fe}_{20}\text{Ni}_{60}\text{P}_{14}\text{B}_6$  results. For  $\text{Fe}_{34}\text{Ni}_{46}\text{P}_{14}\text{B}_6$ , the Curie temperature is high enough  $T = 180^\circ\text{C}$  so that the measurement, which requires about 30 minutes, begins to anneal the sample and influence the result. As a result, this work was not extended to higher iron concentration alloys where the Curie temperature is even higher.

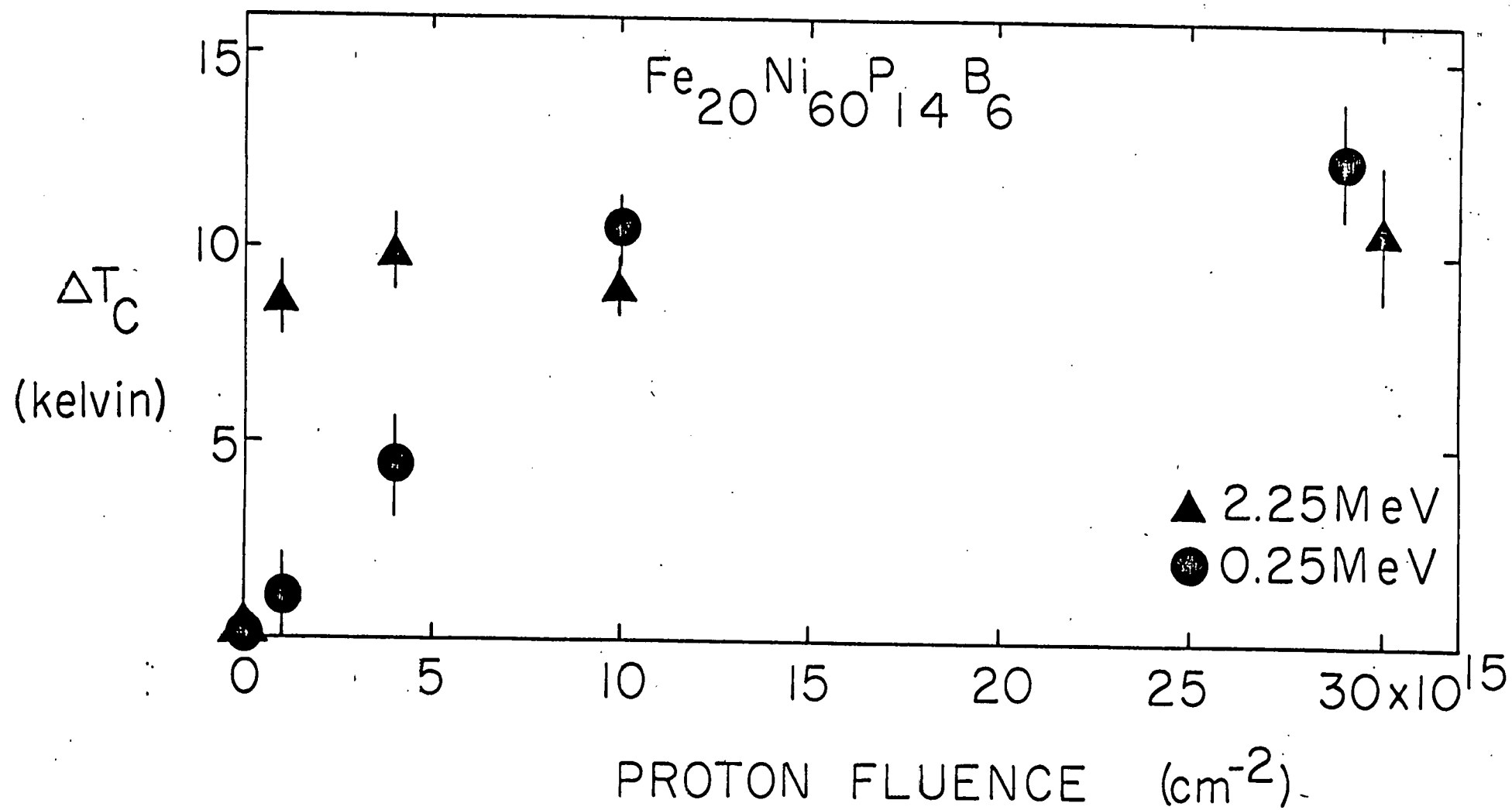


FIG. 1



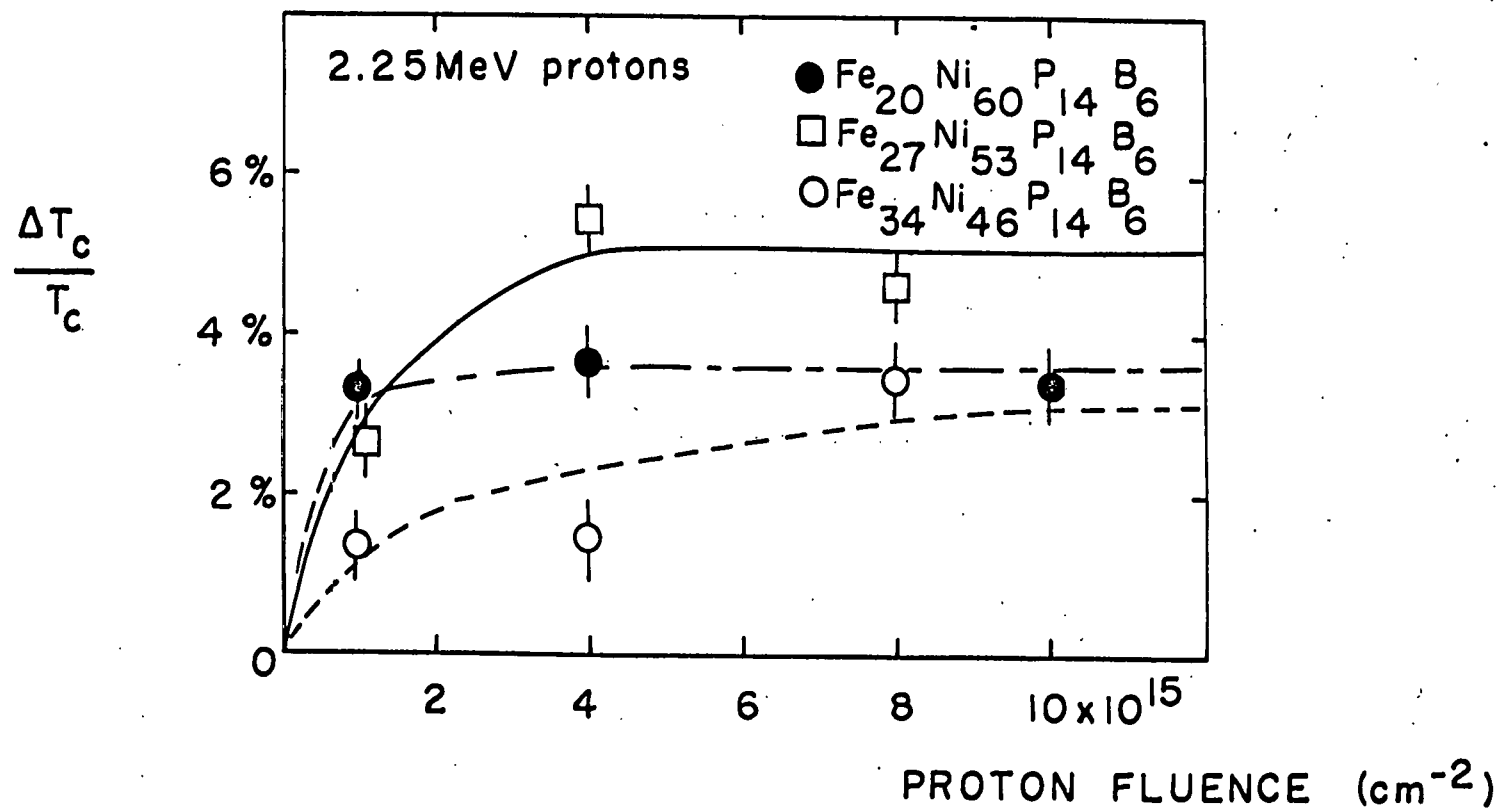


FIG. 2

Measurements of small angle x-ray scattering were conducted on a series of the  $\text{Fe}_{20}\text{Ni}_{60}\text{P}_{14}\text{B}_6$  samples that had been subjected to 2.00 MeV protons. This work was performed at the National Center for Small-Angle Scattering Research, Oak Ridge National Laboratory, Oak Ridge, Tennessee using the Kratky Camera and Copper  $K_\alpha$  radiation. The data collected provided information on the relative number of scattering centers vs. proton fluence (Fig. 3) as well as the size of the scattering centers. The scattering was found to be weak even from the highest fluence sample. Analysis of the angular dependence of the scattering data suggested that the regions responsible for the scattering are small (radius 16 to 30 Å) and that the radius is independent of the fluence. The data follows the same trend observed for the Curie temperature and magnetic saturation change (i.e., the relative intensity reaches a constant value beyond a given fluence level).

#### 4. Complete Construction of Equipment for Electron Irradiations; Perform Series of Electron Irradiations at 2 MeV.

In order to perform electron irradiation some modifications and additions to the University of Delaware 2.5 MeV Van de Graaff accelerator were necessary. An additional beam line and target chamber were constructed. The target chamber has a quartz window at its rear which, when viewed via closed circuit TV, allows for easy and precise electron beam alignment. The sample holder is equipped with a thermocouple and is cooled with compressed air. Cooling will maintain the sample temperature at 33°C while 8 watts of power (typically 1.25 MeV x 6.4  $\mu$ A) is dumped into the copper holder. The analyzing magnet used for protons is also used for electrons; however, it is powered by a different (low voltage) supply. In order to uniformly spread the electron beam over the sample a beam spreader was designed and constructed. Two additional pairs of helmholtz coils placed before the magnet and 3 meters in front of the target sweep the beam horizontally at 60 Hz

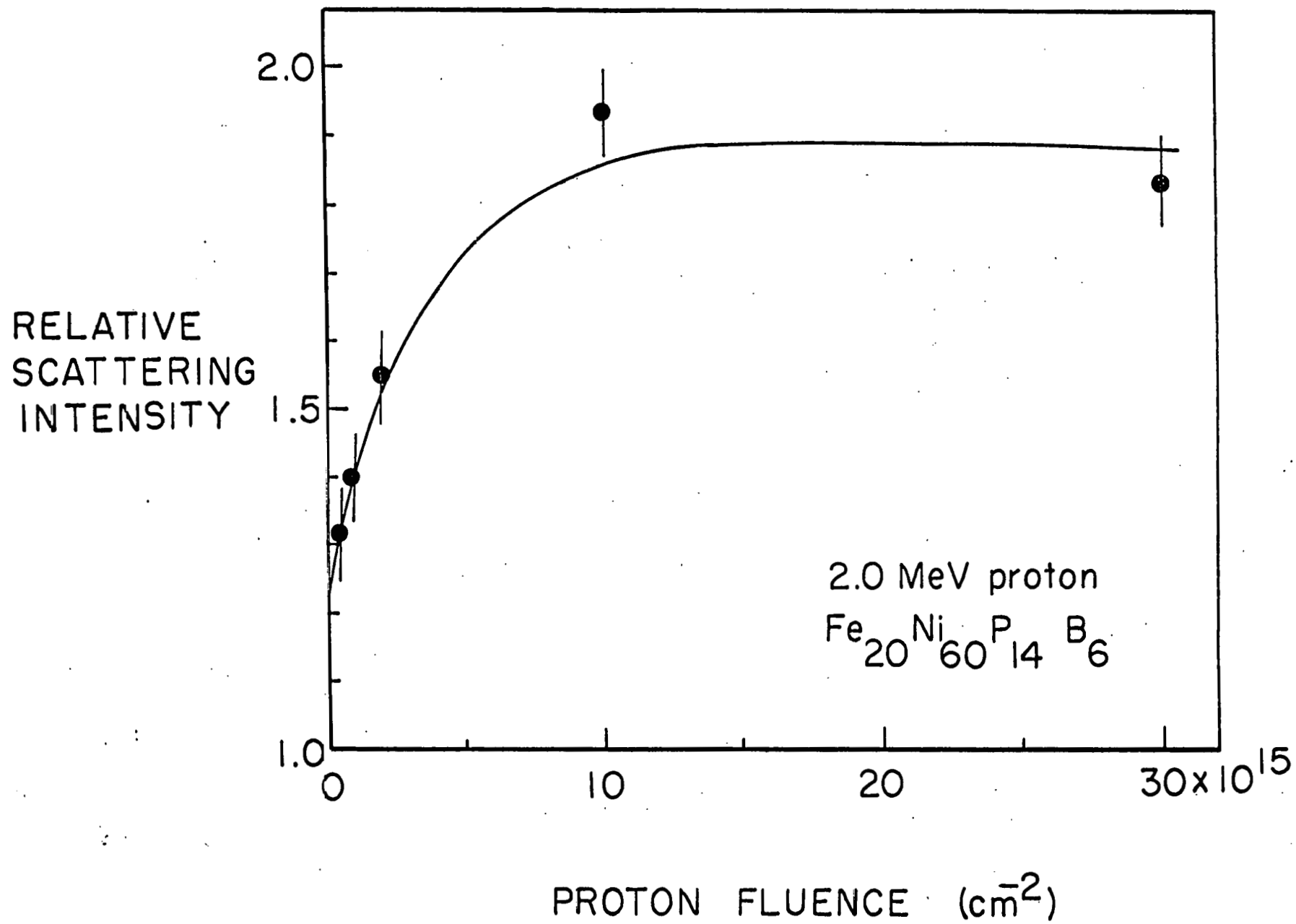


FIG. 3

and vertically at 0.1 Hz. Beam uniformity at the target was verified experimentally.

The results of our first series of 1.25-MeV electron irradiations are shown in Fig. 4.  $\Delta T_c$  is plotted versus electrons per square centimeter in an 11-micron thick sample of  $\text{Fe}_{20}\text{Ni}_{60}\text{P}_{14}\text{B}_6$ .

5. Modify High-Speed Camera for Domain Studies; Develop Techniques of Surface Preparation Necessary for Domain Studies.

The optical system for observing domains via the Kerr magneto-optic technique has been redesigned and necessary optical lenses and prisms have been purchased. The new system is currently being put together. Alignment and evaluation of optical quality will be done using silicon-iron single crystals of known domain structure.

Preliminary domain studies have been conducted on  $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$  alloys using the Bitter pattern technique on polished samples. The domain structure appears to be very complex on the as-manufactured material and requires a combined mechanical and electropolishing procedure to be observed. This procedure also will be used in sample preparation for the Kerr magneto optical studies.

Chemical or electropolishing procedures alone do not remove the undulations and dimples from the original sample surface. The possible impact of mechanical polishing on the domain structure and small angle scattering from the material is expected to be removed by the subsequent electropolishing. The procedure adopted is to mechanical polish using successively finer grits down to  $0.3\mu$ . This is followed by electropolishing using a 50-50 by weight solution of chromic and phosphoric acid with a current density of about  $1.5 \text{ amps/cm}^2$ . Other chemical or electropolishing did not provide as smooth a surface.

Considerable emphasis has been placed on the optical design and sample preparation for domain studies because of the expected complexity of the domain structure and the low optical contrast likely to be observed between domains. The impact of proton

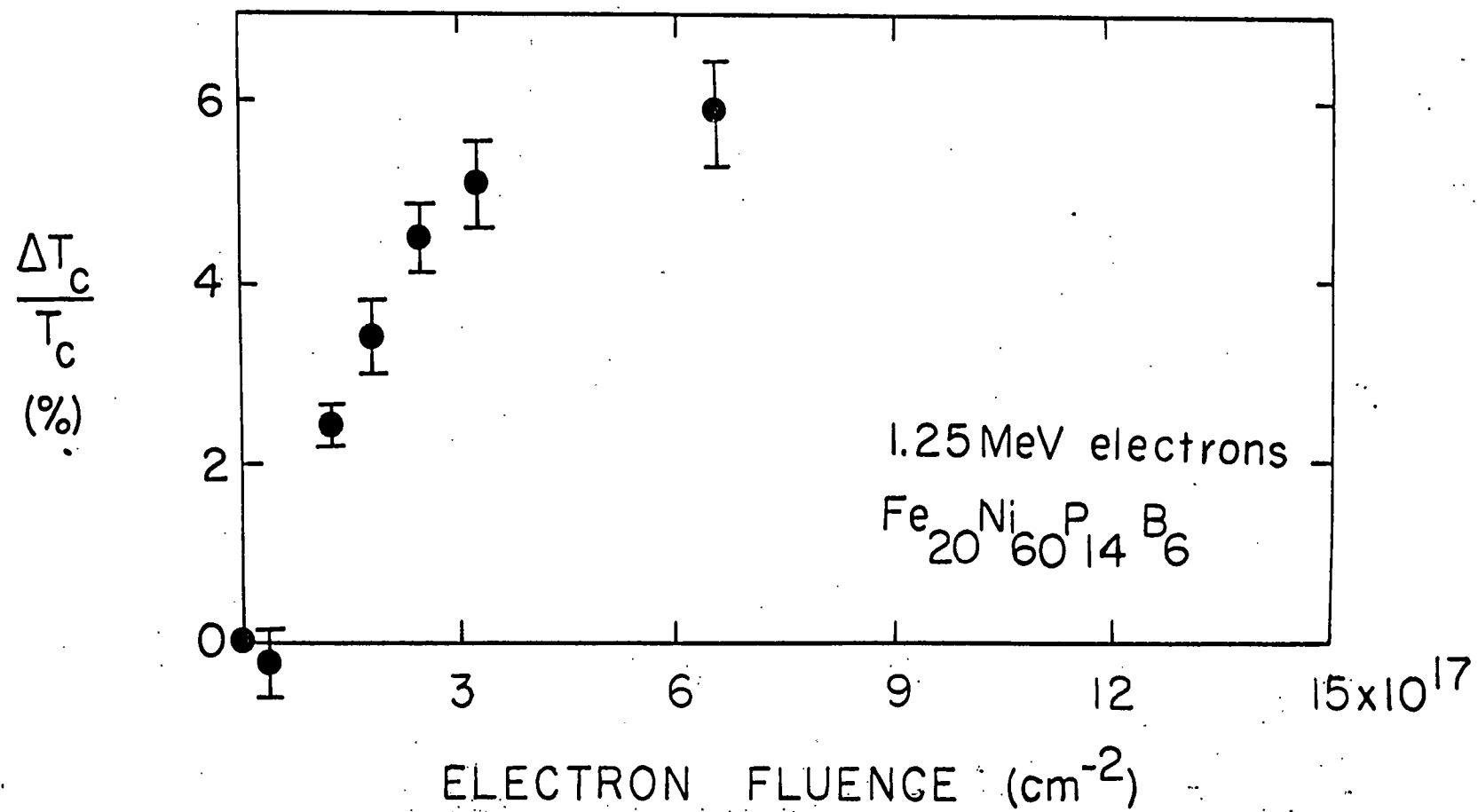


FIG. 4

irradiation on the domain structure and dynamics will be investigated by initially observing the domains in a selected region of a polished sample and subsequently making the same observations in this region following proton irradiation. This should minimize any unexpected effects due to surface preparation.

6. Complete Construction of Low-Temperature Electrical Resistivity Apparatus

In the original proposal we noted that a 4-probe electrical resistivity cryostat had been completed. Initial experience with this equipment was unsatisfactory as the design did not allow adequately for sample thermal expansion, thus subjecting the sample to strain. We have since redesigned the cryostat to correct this problem and also to allow for rapid sample change-over and for full automation of data-taking. We anticipate that the new system will be operational by the end of the first funding year.

7. Initiate Construction of High-Temperature Resistivity Apparatus

Drawings have been submitted to the shop. Heater design is complete. Sample holder and electrical contact mechanism is in design stage at this time.

8. Initiate Measurements on Magnetic and Electrical Properties (Including Domain Studies) and Small-Angle X-ray Scattering.

Results obtained to date are presented in section 3 above. A tentative interpretation of the results is given as follows:

First, it appears that hydrogen implantation is not contributing significantly to the observed effects. In Fig. 1 it is seen that, at low fluences, high energy protons induce a larger  $\Delta T_c$  than for the low energy proton case. The high-energy beam completely penetrates that sample while the low-energy beam is stopped in the target (implanted). Furthermore, electron irradiation produces a similar  $\Delta T_c$  (see Fig. 4).

Second, we can calculate the number of displacements per atom (dpa) of the target from Kinchin-Pease theory for both electrons and protons, assuming a displacement energy of 25 eV. Converting the abscissas of Figs. 1 and 4 to dpa we obtain a composite figure for both electrons and protons in Fig. 5. Two

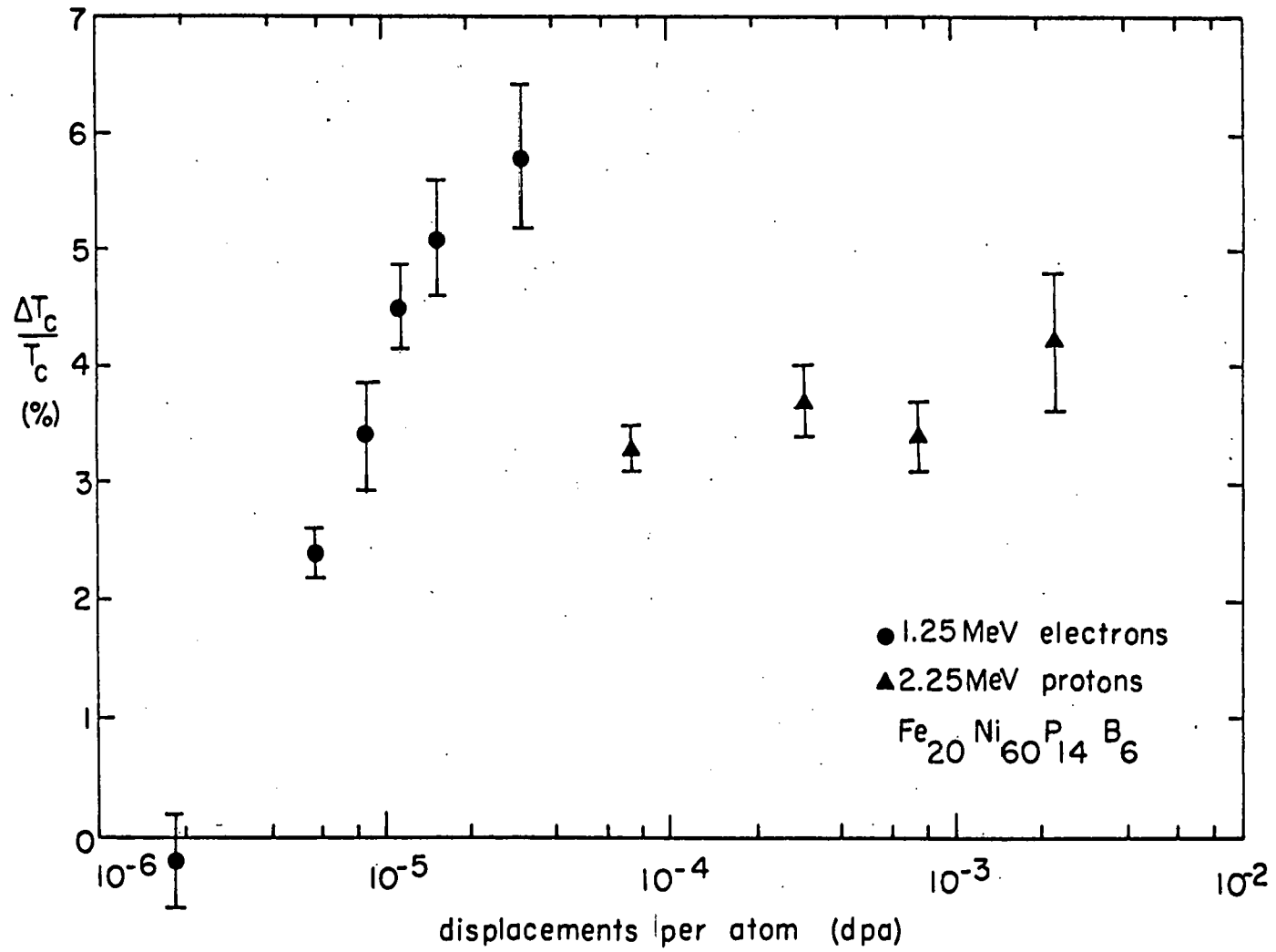


FIG. 5

important points are noted: (a) Electron and proton results do not scale together at all, (b) Significant values of  $\Delta T_c/T_c$  are observed at surprisingly low values of dpa, of order  $10^{-4}$  to  $10^{-5}$ . These observations suggest that the observed effects do not arise from atomic displacements.

Finally, we can convert the abscissas of Figs. 1 and 4 to energy deposited per  $\text{cm}^3$  of target, see Fig. 6. This figure includes  $T_c$  data from electron irradiation and 2.25 MeV protons and data from  $M(\text{sat})$  measurements. (The factor of 2 arises from a molecular field model and allows us to compare fractional changes in  $M(\text{sat})$  directly with those in  $T_c$ ). We note that there is reasonably good scaling of all 3 sets of data.

Based on the above we tentatively conclude that the observed changes in  $T_c$ ,  $M(\text{sat})$  and x-ray scattering intensity are due to the effects of localized energy deposition in the particle tracks. Such effects are widely discussed in the literature (see, e.g. Vineyard, Ref. 1) and may result in radiation-enhanced diffusion of one of the target constituents. In the alloys studied here, diffusion of phosphorous to form clusters is a distinct possibility. This is further suggested by the analogy between radiation effects observed in this work and thermal annealing effects observed elsewhere (2).

#### Summary of Results in First Year

Equipment has been constructed to permit measurement of Curie temperatures in the range  $77^\circ\text{K}$  to  $650^\circ\text{K}$ . A melt-spinner has been constructed and ribbons of  $\text{Fe}_x\text{Ni}_{80-x}\text{P}_{14}\text{B}_6$  have been fabricated for  $x = 20, 27, 34$ . A beam line, target chamber and necessary electronics have been put together for electron irradiation. A series of proton irradiations has been carried out on all 3 ribbons with protons of low energy that are implanted in the sample and with protons of high energy that completely penetrate the sample. A series of electron irradiations at 1.25 MeV has been performed on the  $\text{Fe}_{20}$  sample. Results show an increase in saturation magnetization as measured at  $77^\circ\text{K}$ , an increase in Curie temperature, and an increase in small-angle



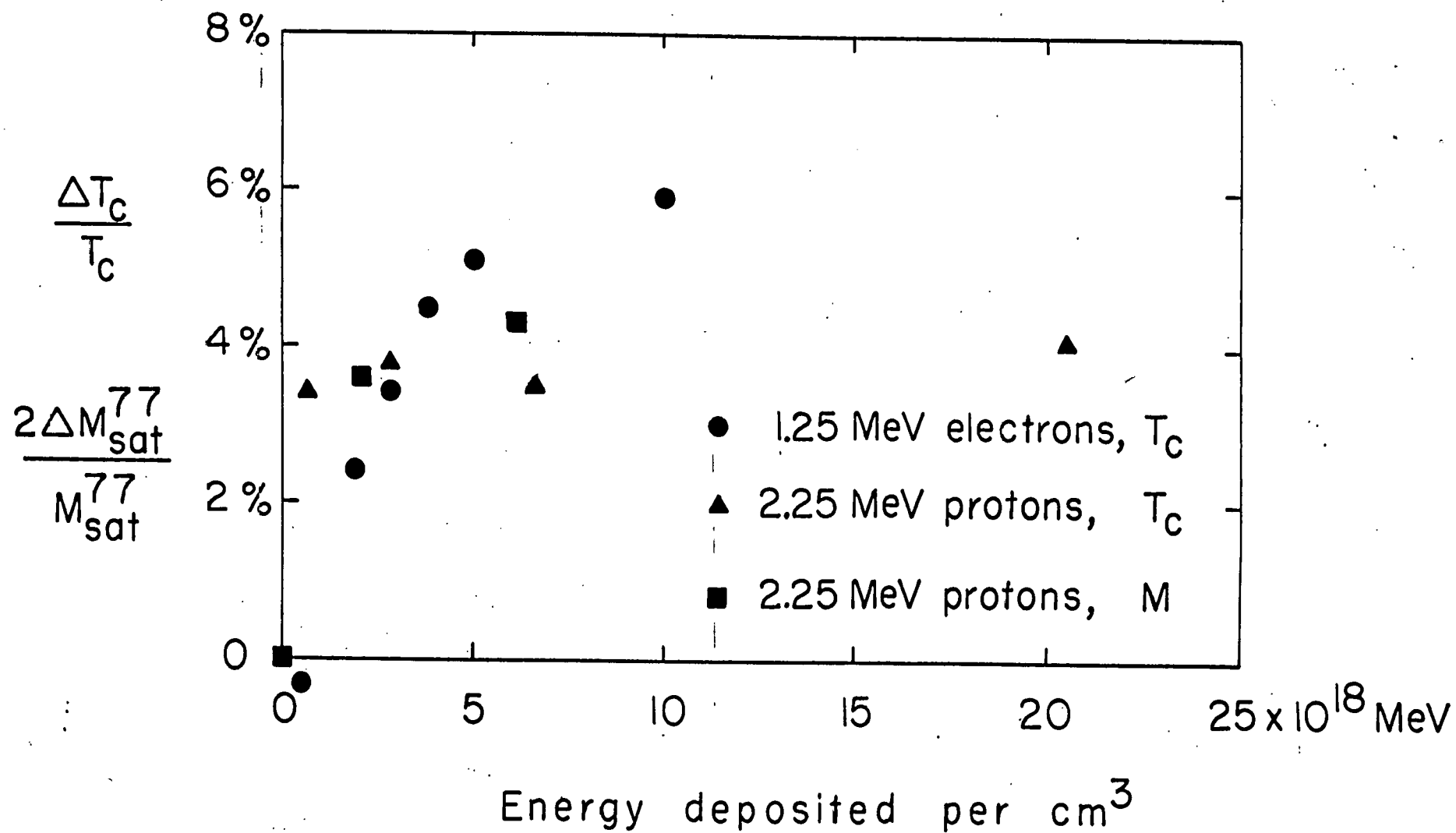


FIG. 6

x-ray scattering. All of these functions rise to a maximum value as a function of particle fluence and then remain constant with further irradiation. Analysis of the data reveals that hydrogen implantation does not play a significant role. The data indicate that the important variable is energy deposited, suggesting that the observed effects are due to localized energy deposition in the projectile path, perhaps radiation-enhanced diffusion of phosphorous.

Equipment has been assembled and techniques are being refined to permit magnetic domain studies. Equipment has been designed and is under construction for measurement of electrical resistivity from helium temperature through the crystallization region.

Two publications of results from this research program are attached to this report.

Radiation effects in amorphous  $\text{Fe}_{x-80-x}\text{Ni}_{14}\text{P}_{14}\text{B}_6$ 

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## ABSTRACT

Changes in the Curie temperature and magnetic saturation of the amorphous ferromagnetic series  $\text{Fe}_{x-80-x}\text{Ni}_{14}\text{P}_{14}\text{B}_6$  for  $20 \leq x \leq 34$  induced by proton bombardment have been studied, and correlated with small angle x-ray scattering measurements performed for  $x = 20$  at Oak Ridge National Laboratory. Both the Curie temperature and the low temperature saturation magnetization increase with proton fluence up to

$10^{16} \text{ cm}^{-2}$  but are constant for higher fluences. Protons of energy 2.25 MeV (range much greater than the sample thickness) are more effective at producing changes than protons of energy 0.25 MeV (range much less than sample thickness). Thus, hydrogen implantation is eliminated as the principal source of the observed changes. In addition, careful attention to sample temperature during irradiation excludes thermal annealing as the origin of the effect.

Proton bombardment at the same fluences produces scattering centers that are observed by small angle x-ray scattering. The concentration of scattering centers increases with proton fluence up

to  $10^{16} \text{ cm}^{-2}$ , but remains constant thereafter. The size of the centers remains constant at about 16-30 Å.

Possible structural changes to account for these observations are incipient recrystallization, void formation, and phosphorous segregation.

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## INTRODUCTION

Proton bombardment of crystalline materials at fluences of  $10^{15} - 10^{16} \text{ cm}^{-2}$  is known to create radiation damage, principally in the form of vacancies and interstitials, which can be detected by optical absorption, spin resonance or resistivity measurements depending on the properties of the material (1). Also, hydrogen implantation could have an effect if the proton range is less than the material thickness (2). Similar irradiation of amorphous materials might be expected to cause some changes in the material, but precisely what form this would take is not known. However, it seems likely that proton damage will be manifested directly or indirectly in at least one of the following effects: 1) hydrogen implantation, 2) crystallization, 3) free volume production, 4) local and macroscopic heating, and 5) segregation of constituent elements.

In order to determine if and which of these effects may be occurring, a series of measurements to detect possible changes in the Curie temperature, saturation magnetization, and small angle x-ray scattering of the amorphous series  $\text{Fe}_{80-x}\text{Ni}_x\text{P}_{14}\text{B}_6$  for  $20 \leq x \leq 34$  have been made. This series has been chosen because the alloys are ferromagnetic and the above measurements can be made without annealing the samples in the process.

## EXPERIMENTAL MEASUREMENTS

It is well known that annealing can significantly alter the magnetic properties of amorphous alloys (3). Therefore, care has been exercised to control the sample temperature during irradiation so that measured changes are truly radiation caused changes. Ribbons of  $\text{Fe}_{80-x}\text{Ni}_x\text{P}_{14}\text{B}_6$  prepared by single wheel spin quenching (thickness  $11 \pm 2 \mu\text{m}$ ) were wrapped continuously around a copper block of dimension  $25 \text{ mm} \times 25 \text{ mm} \times 6 \text{ mm}$  such that one  $25 \text{ mm} \times 25 \text{ mm}$  face was open to the proton beam during bombardment. The ribbons were subsequently cut from the block, leaving twenty  $25 \text{ mm}$  strips of ribbon from each  $25 \text{ mm} \times 25 \text{ mm}$  face. This technique enables the irradiation of every other inch of a ribbon, with the alternate  $25 \text{ mm}$  strips serving as virgin control samples which have had the same thermal history. This tends to minimize both thermal annealing effects on the measurements and trends in the data from gradual

variations in composition along the length of the ribbon. To further minimize any annealing effects, beam currents were kept low (400 nA over 25 mm x 25 mm) so that the sample temperature never exceeded 40°C during irradiation, as measured by a thermocouple attached to the ribbon.

Samples of  $\text{Fe}_{20}\text{Ni}_{60}\text{P}_{14}\text{B}_6$  were bombarded with protons of energy 2.25 MeV (range greater than sample thickness) and 0.25 MeV (range less than sample thickness). Resultant changes in Curie temperature with proton fluence are shown in Fig. 1, indicating the difference in effect between bombardments of these two energies. Curie temperature measurements were made in a 60 Oe, 407 Hz ac field, rather than the customary vibrating sample in a dc field method. Measurements made by this technique agree quite well with those reported elsewhere (3). The saturation magnetic moment of these samples was measured and found to increase at a fractional rate of one-half the increase in Curie temperature.

Using the same technique, samples of  $\text{Fe}_{27}\text{Ni}_{53}\text{P}_{14}\text{B}_6$  and  $\text{Fe}_{34}\text{Ni}_{46}\text{P}_{14}\text{B}_6$  were bombarded with 2.25 MeV protons. The resultant changes in Curie temperature are shown in Fig. 2 along with the 2.25 MeV  $\text{Fe}_{20}\text{Ni}_{60}\text{P}_{14}\text{B}_6$  results. For  $\text{Fe}_{34}\text{Ni}_{46}\text{P}_{14}\text{B}_6$ , the Curie temperature is high enough ( $T_c = 180^\circ\text{C}$ ) so that the measurement, which requires about 30 minutes, begins to anneal the sample and influence the result. As a result, this work was not extended to higher iron concentration alloys where the Curie temperature is even higher.

Measurements of small angle x-ray scattering were conducted on a series of the  $\text{Fe}_{20}\text{Ni}_{60}\text{P}_{14}\text{B}_6$  samples that had been subjected to 2.00 MeV protons. This work was performed at the National Center for Small-Angle Scattering Research, Oak Ridge National Laboratory, Oak Ridge, Tennessee using the Kratky-Camera and Copper  $K_\alpha$  radiation. The data collected provided information on the relative number of scattering centers vs. proton fluence (Fig. 3) as well as the size of the scattering centers. The scattering was found to be weak even from the highest fluence sample. Analysis of the angular dependence of the scattering data suggested that the regions responsible for the scattering are small

(radius 16 to 30 Å) and independent of the level of

fluence. The data follows the same trend observed for the Curie temperature and magnetic saturation change (i.e., the relative intensity reaches a constant value beyond a given fluence level).

#### DISCUSSION

The observed changes in the magnetic properties and small-angle scattering with proton irradiation strongly suggests that events are occurring that are more complex than the individual vacancy and interstitial events that are known to occur in crystalline material. Irradiation effects, however, are known to occur in crystalline magnetic materials resulting in properties changes that cannot be explained by simple consideration of random vacancy and interstitial formation. Nickel-iron alloys (50-80% Ni) subject to neutron irradiation at room temperature show an induced directional order in each of the magnetic domains (4). This observed phenomenon has been attributed to a diffusion enhancing effect of the radiation, resulting in long-range order. Such enhanced diffusion, however, is likely due to interstitial and vacancy formation.

In the case of the amorphous alloy the proton irradiation can be expected to give rise to local regions of excess "free volume," (analogous to crystalline vacancies) which could result in enhanced diffusion in the amorphous alloy. Swelling of the amorphous alloy  $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$  as the result of nickel ion radiation has been reported (5). It would certainly be possible for protons to produce the same type of regions.

Enhanced diffusion could result in a number of possible changes in the amorphous alloy. It is anticipated that changes will occur in a direction leading to thermodynamic equilibrium. For these series of alloys the ultimate condition following high temperature treatment is a crystallized structure of  $\text{Fe}_3\text{P}$ ,  $\text{Ni}_3\text{P}$ , and other compounds (6).

In addition, some investigation has been conducted on the sequence of reactions occurring during the crystallization process of these alloys. In particular, the early stages of annealing seem to be associated with phosphorus segregation, as deduced from small-angle scattering measurements and Auger analysis of fractured surfaces.

It is well known that annealing also gives rise to changes in the Curie temperature of this series of alloys. Such changes occur before the

onset of crystallization and are in the direction of increased Curie temperature during the early stages of anneal. (3) Measurements made here on  $\text{Fe}_{27}\text{Ni}_{53}\text{P}_{14}\text{B}_6$  agree with this. The maximum change in the Curie temperature observed following heat treatment at  $200^\circ\text{C}$  is equal to the maximum change observed as a result of irradiation.

Additional similarities also exist between the irradiated and the annealed samples. Both are embrittled as a result of the respective treatments. Furthermore, changes in the Curie temperature resulting from a two stage process of initial radiation followed by an anneal do not result in Curie temperature changes beyond that which can be obtained by an anneal alone, or a radiation dosage greater than  $10^{16} / \text{cm}^2$  of 2.25 MeV protons (to be reported later).

Some comparison can be made between the small-angle scattering results for the irradiated samples measured here and measurements made by Walter, Legrand, and Luborsky for  $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$  following annealing (7). In both cases the size of the scattering particles is small (i.e., 20-30 Å). Their increase in the number of particles on annealing, however, appears to be somewhat greater than the increase measured here following irradiation for the high fluence level. Since the total number of scattering centers is small, the number of scattering events is proportional to the number of scattering centers, if corrections for absorption and background are made. Their maximum increase for the annealed samples is reported to be a factor of three over the unannealed samples which also show scattering. For the case of the irradiated samples measured here, the increase was found to be a factor of two (Fig. 3). Small-angle scattering measurements of a single sample of  $\text{Fe}_{20}\text{Ni}_{60}\text{P}_{14}\text{B}_6$  investigated here after annealing for 4 hrs. at  $200^\circ\text{C}$ , however, resulted in an increase of scattering by a factor of about two. These annealing conditions also give rise to the maximum change in the Curie temperature.

Phosphorous segregation is consistent with the direction of change of the Curie temperature. For FeNiPB alloys with the same iron and nickel concentration, the Curie temperature increases with decreasing phosphorous concentration (8). Thus, if phosphorous were being removed from the host material to clusters, the chemical surroundings of the remaining atoms would favor higher Curie temperature.

The origin of the saturation effect is not known. It is estimated that the amount of scattering observed is not consistent with all of the phosphorous combined into clusters. Changes in small-angle scattering following thermal annealing are found to saturate in the Walter, Legrand, and Luborsky work, as well. They reported scattering centers make up only 1-2% of the total volume (7).

#### CONCLUSION

Hydrogen implantation does not appear to contribute significantly to the observed changes. If it did, the 0.25 MeV protons would have been more effective than the 2.25 MeV protons in producing changes. Figure 1 shows the opposite to be true.

The observed changes in Curie temperature, saturation magnetic moment, and small-angle x-ray scattering are of the same order of magnitude as changes induced by thermal annealing. However, experimental procedure has eliminated the possibility of the observations being induced by macroscopic heating of the sample. Localized heating in the immediate vicinity of the proton tracks may, however, be responsible. It has been reported that extremely high temperatures may be achieved for short periods of time (9) which result in localized melting and subsequent reformation of the material in an alternate structure.

It is suggested then, that the effect of the proton irradiation is to produce enhanced diffusion, probably due to excess "free volume" coupled with localized heating, which results in the migration of phosphorous to clusters, leading to the experimental observations.

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