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Radiation effects in amorphous $Fe_xNi_{80-x}P_{14}B_6$

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ABSTRACT

Changes in the Curie temperature and magnetic saturation of the amorphous ferromagnetic series $Fe_xNi_{80-x}P_{14}B_6$ 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} 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} 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 $10^{15} - 10^{16} cm^{-2}$ 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 matertial 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 an 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 $Fe_xNi_{80-x}P_{14}B_6$ 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 $Fe_xNi_{80-x}P_{14}B_6$ 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 $Fe_{20}Ni_{60}P_{14}B_6$ 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 $Fe_{27}Ni_{53}P_{14}B_6$ and $Fe_{34}Ni_{46}P_{14}B_6$ were bombarded with 2.25 MeV protons. The resultant changes in Curie temperature are shown in Fig. 2 along with the 2.25 MeV $Fe_{20}Ni_{60}P_{14}B_6$ results. For $Fe_{34}Ni_{46}P_{14}B_6$, the Curie temperature is high enough T_c = 180°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 $Fe_{20}Ni_{60}P_{14}B_6$ 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_α 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 $Fe_{40}Ni_{40}P_{14}B_6$ 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 Fe_3P, Ni_3P, 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 segragation, 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 $Fe_{27}Ni_{53}P_{14}B_6$ agree with this. The maximum change in the Curie temperature observed following heat treatment at 200°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} / 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 $Fe_{40}Ni_{40}P_{14}B_6$ 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 $Fe_{20}Ni_{60}P_{14}B_6$ investigated here after annealing for 4 hrs. at 200°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 nickle 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.

REFERENCES

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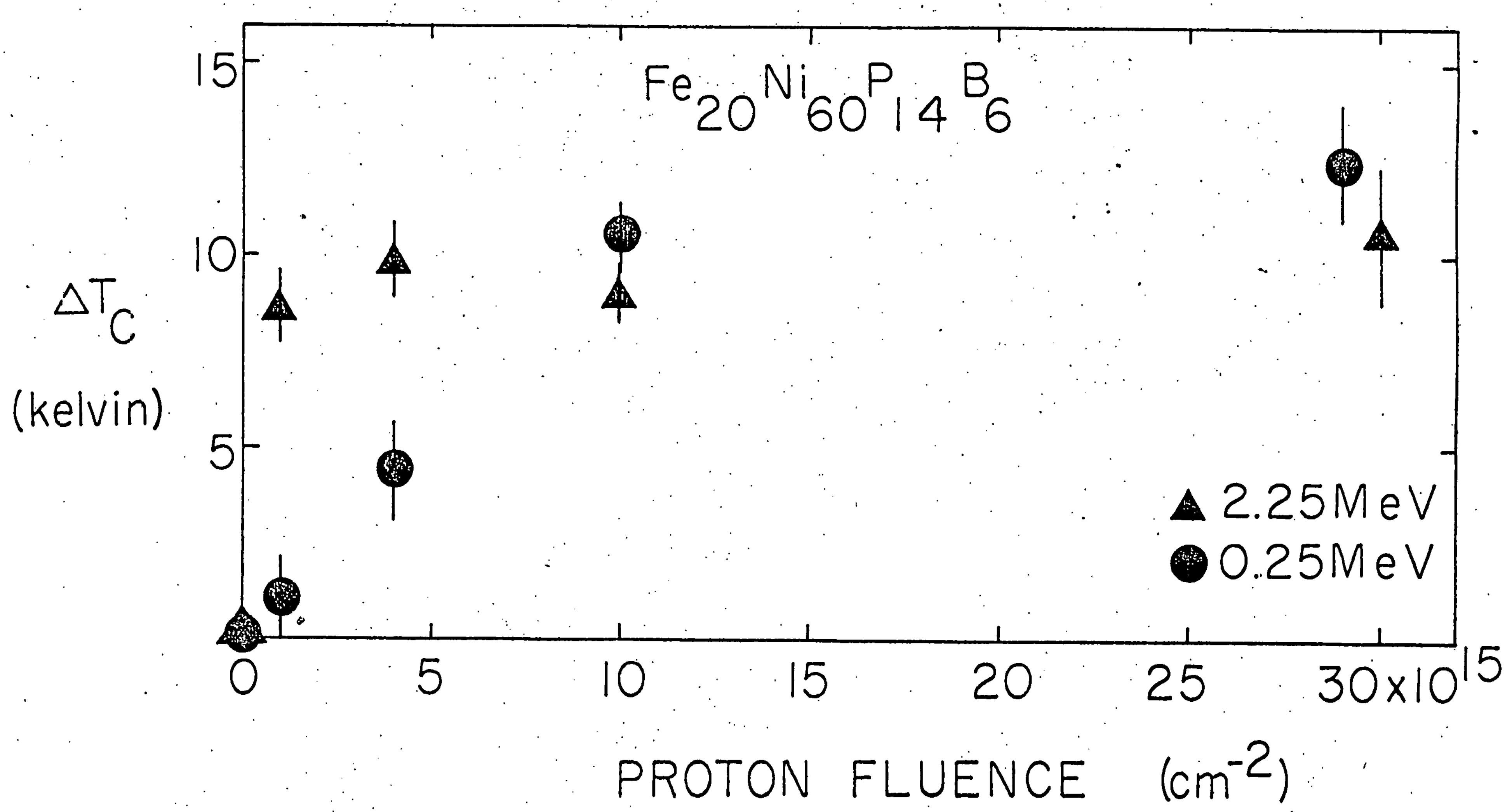


Fe20Ni60P14B6
ΔTC
(kelvin)
15
10
5
0
5
10
15
20
25
30x10^15
PROTON FLUENCE (cm^-2)
2.25MeV
0.25MeV

FIG. 1

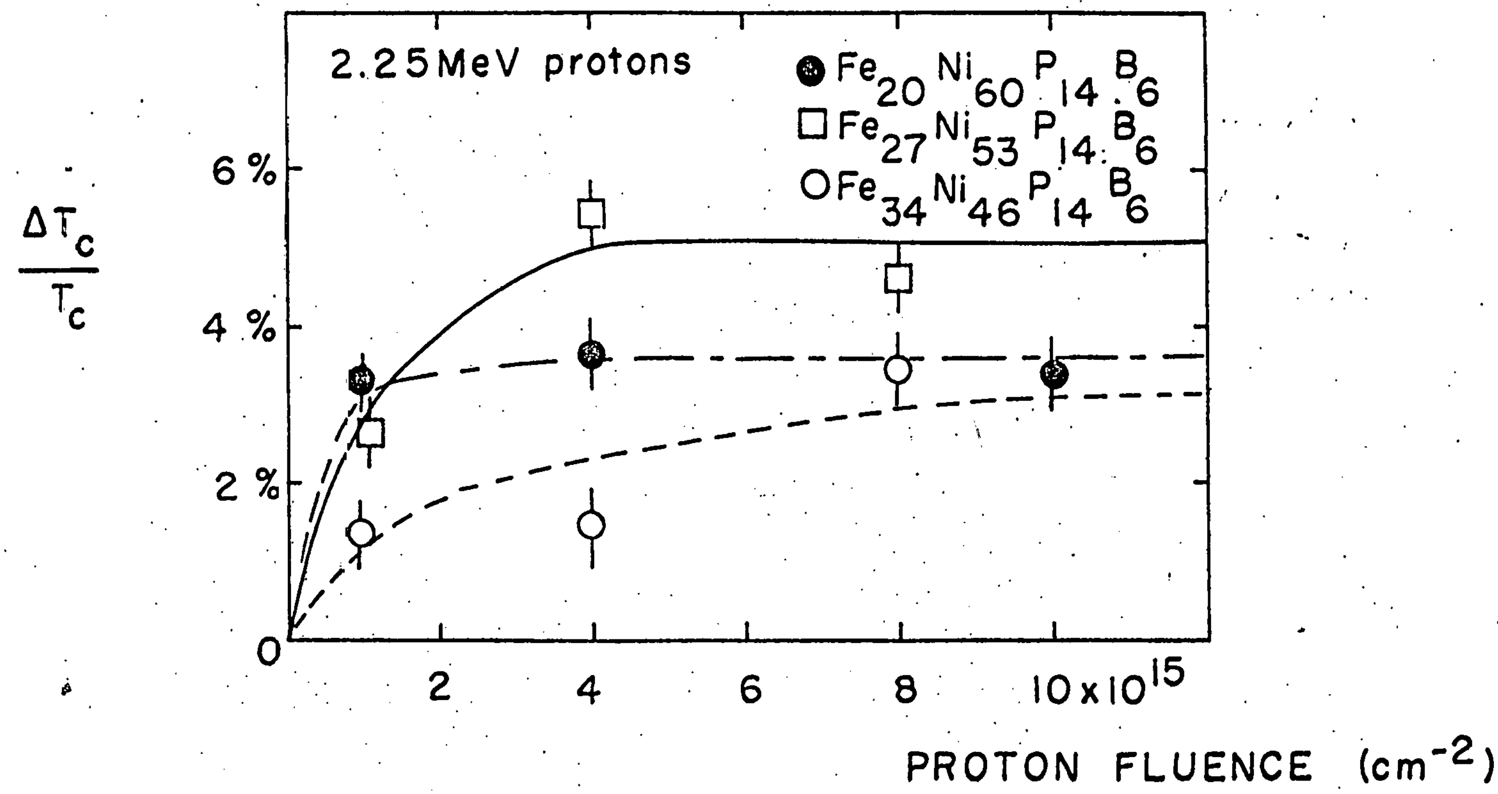
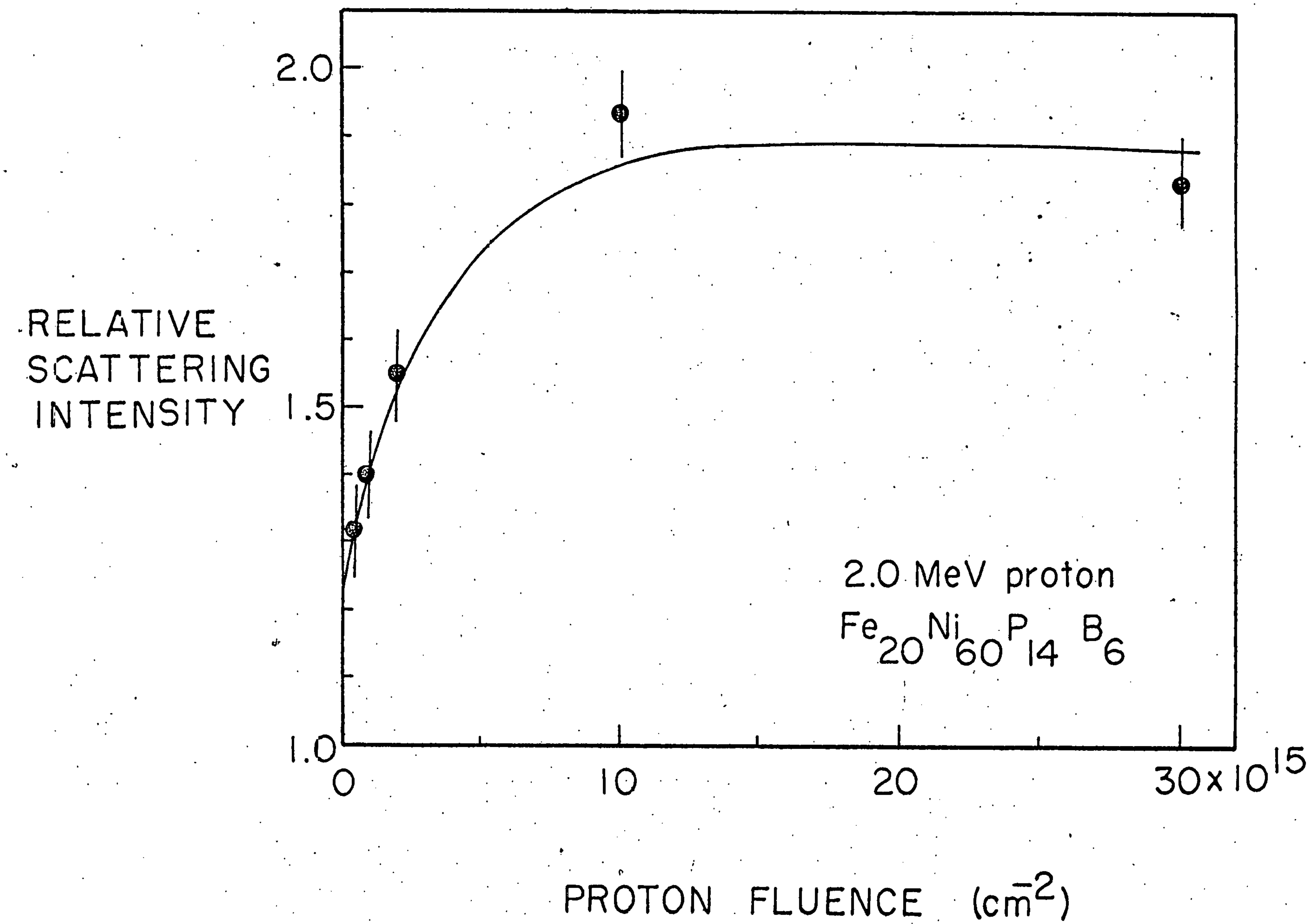

2.25 MeV protons
Fe20 Ni60 P14 B6
Fe27 Ni53 P14 B6
Fe34 Ni46 P14 B6
ΔTc / Tc
6 %
4 %
2 %
0
2
4
6
8
10x10^15
PROTON FLUENCE (cm^-2)

FIG. 2



RELATIVE SCATTERING INTENSITY
2.0
1.5
1.0
0
10
20
30x10^15
2.0 MeV proton
$Fe_{20}Ni_{60}P_{14}B_{6}$
PROTON FLUENCE (cm^{-2})

FIG. 3