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HIGH-ENERGY NEUTRON IRRADIATION OF SUPERCONDUCTING COMPOUNDS*

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ABSTRACT

The effect of high-energy neutron irradiation (E>1 MeV) at ambient reactor temperatures on the superconducting properties of a variety of superconducting compounds is reported. The materials studied include the A-15 compounds Nb_3Sn, Nb_3Al, Nb_3Ga, Nb_3Ge and V_3Si, the C-15 Laves phase HfV_2, the ternary molybdenum sulfide $Mo_3Pb_{0.5}S_4$ and the layered dichalcogenide $NbSe_2$. The superconducting transition temperature has been measured for all of the above materials for neutron fluences up to 5×10^{19} n/cm^2. The critical current for multifilamentary Nb_3Sn has also been determined for fields up to 16 T and fluences between 3×10^{17} n/cm^2 and 1.1×10^{19} n/cm^2.

INTRODUCTION

In most present designs for fusion reactors superconducting magnets will be utilized to provide plasma confinement. In such an application the superconductor will be subjected to neutron irradiation, the exact level depending on the particular design and length of exposure.[1] It

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is therefore necessary to have information concerning the effect of such radiation on the superconducting properties of potential magnet material, particularly the effect on the superconducting transition temperature T_c and the critical current density J_c.

In this work we report the effect of high-energy neutron (E>1 MeV) irradiation at ambient reactor temperatures on the superconducting properties of a variety of intermetallic compounds that have potential use for high-field magnets. Although the neutrons produced in a fusion vessel will have energies of ~14 MeV, by the time they reach the region where the magnets will be located, their energy is expected to be ~1 MeV with a spectrum similar to that of a fission reactor.[2] It is therefore possible to gain meaningful information concerning the behavior of superconducting materials to be used in fusion reactors by irradiation with neutrons from a fission reactor.

The materials studied here include the A-15 compounds Nb_3Sn, Nb_3Ga, Nb_3Ge, Nb_3Al and V_3Si. Nb_3Sn has been developed into multifilamentary conductors for magnet use[3] and besides the effect of neutron irradiation on T_c, extensive J_c data, up to fields of 16 T and fluences of $\sim 10^{19}$ n/cm^2, are reported. Nb_3Ga has also been developed into usable form for magnet construction[4] and the effect on T_c up to fluences of 5.0×10^{19} n/cm^2 is also reported. Nb_3Ge, currently possessing the highest T_c, ~23 K,[5] of any known superconductor is investigated up to fluences of 5.0×10^{19} n/cm^2 and annealing experiments to 900°C are described.

Other compounds studied include the ternary molybdenum sulfide $Mo_3Pb_{0.5}S_4$,[6] which has the highest reported upper critical field of any bulk material, ~50 T[7] making it extremely desirable for magnet use if it could be prepared so as to carry reasonable currents, a prospect not yet realized.[8] The C-15 Laves phase HfV_2, and pseudobinary compounds with Zr having this structure, also are potential magnet conductors as J_c's as high as 10^5 A/cm^2 at 13 T at 4.2 have been obtained[9] despite its relatively low T_c of 10 K. These materials are also less brittle than the A-15's, making wire and tape fabrication somewhat easier. Finally we mention the layered dichalcogenide $NbSe_2$ even though it is not a good candidate for magnet material to show how neutron-induced disorder can be correlated with disorder brought about by deintercalation.

EXPERIMENTAL

The characteristics of the samples before irradiation along with the preparative techniques are listed in Table 1. The irradiations were carried out in the Brookhaven High Flux Beam Reactor (HFBR), the fluence being obtained by multiplying the time of irradiation by the fast flux (E>1 MeV) which is known to be $(1.0\pm0.5)\times10^{14}$ n/cm^2 sec. The measured temperature of the samples during irradiation was 140°C. T_c was measured inductively in a manner previously[15] described and J_c determined by noting the current at which a 3-μV signal appeared across the superconductor.[16]

RESULTS AND DISCUSSION

Transition Temperatures

Figure 1 shows the effect of high-energy neutron irradiation on the T_c's of the various materials used in this work. T_c is the value after irradiation and T_{co} is the value before irradiation listed

Table 1. Sample Characteristics Before Irradiation

Sample	Transition Temp. T_{co}(K)	Lattice Parameter a_0(Å)	Method of Preparation	Comments
Nb_3Ge	20.6	5.142	Ref. 10	Chemically vapor deposited. ~70% A-15 + Nb_5Ge_3 phase
Nb_3Ga	20.3	5.165	Ref. 11	A-15 + ~50% Nb_5Ga_3 phase
Nb_3Al	18.7	5.183	Ref. 12	>98% single phase
Nb_3Sn	18.1	5.290	Ref. 13	Used for T_c measurements - single phase
Nb_3Sn	15.0		Ref. 3	19 core multifilamentary conductor J_c=1.0x10^6 A/cm^2 at 4 T
V_3Si	17.1			Single phase - arc cast
$Mo_3Pb_{0.5}S_4$	13.0		Ref. 6	Sintered powder compacts
HfV_2	9.4		Arc cast	
$NbSe_2$	7.1	a=3.45 c=12.56	Ref. 14	Double layer hexagonal type

in Table 1. The data are presented on a normalized plot to indicate the relative change in T_c as a function of fluence.

The materials most extensively studied are those having the A-15 (β-W) structure Nb_3Ge, Nb_3Al, Nb_3Sn, Nb_3Ga and V_3Si. When plotted on a normalized plot we see that the depressions in T_c due to the neutron irradiation are very similar for the Nb-base A-15 compounds. Up to $\sim10^{18}$ n/cm^2 there is very little change in T_c ~4-6% relative to the unirradiated value. Above this fluence, T_c begins to be rapidly depressed. For fluences $\sim5\text{x}10^{18}$ n/cm^2 T_c has been decreased by ~20%, for $\sim10^{19}$ n/cm^2 ~40% and above 10^{19} n/cm^2 reductions greater than 90% in T_c are observed. In the case of Nb_3Al no superconductivity was observed for fluences $>1\text{x}10^{19}$ n/cm^2 to a temperature of 1.2 K and recent data indicate that at $5\text{x}10^{19}$ n/cm^2 Nb_3Ge also shows no superconductivity to 1.2 K.[17] V_3Si lies somewhat below the curve for the Nb-based A-15 compounds at fluences below 10^{19} n/cm^2 indicating that the relative depression of T_c for this material is somewhat greater than for the Nb A-15 compounds.

The large depressions in T_c shown in Fig. 1 for the A-15 materials are due to replacement collisions brought about by the fast-particle irradiation resulting in a decrease in the degree of long-range order.[18] This has been confirmed directly in the case of Nb_3Al where measurements of the degree of long-range order before and after irradiation showed the order to decrease with increasing neutron dose.[12] We also note that with respect to T_c both low-temperature irradiations (30 K)[19] and ambient-temperature irradiations (140°C) give similar depressions in T_c for Nb_3Sn. In both cases the results are well described by a siteexchange-disorder model yielding depression rates of 2-3 K per percent of B atom on the Nb chains in the A-15 structure.

The ternary molybdenum sulfides have recently been prepared with T_c's in the range 10-13 K[6] and upper critical fields of the order 50 T[7] have been reported. The extremely high critical fields and reasonably high T_c's make these materials attractive as potential magnet materials. However, recent attempts to fabricate the sulfides into usable conductors have resulted in rather low current densities, $\sim 10^3$ A/cm^2 at 4 T.[8] Whether these low J_c values are inherent to the material or are the result of the preparative techniques employed to prepare the material in conductor form is not known.

Figure 1 shows the effect of neutron irradiation on the T_c of $Mo_3Pb_{0.5}S_4$. We see immediately that T_c is extremely sensitive to neutron bombardment at all fluences studied. Even at the relatively low fluence of 5×10^{17}, T_c is depressed by 8% relative to its unirradiated value. At 10^{18} n/cm^2 T_c is down by 22% compared to the A-15 compounds whose T_c has decreased by only about 6%. At levels close to 10^{19} n/cm^2 no superconductivity was detected to 4.2 K, indicating a depression in T_c of >65%. We thus see that the T_c of $Mo_3Pb_{0.5}S_4$ is quite sensitive to neutron irradiation. Although we have not made any crystallographic measurements to determine the changes taking place in the structure during irradiation, as with the A-15's, the superconducting properties of the ternary molybdenum sulfides are known to be extremely sensitive to pressure and strain and thus it is not surprising that T_c would be sensitive to heavy-particle irradiation.

$NbSe_2$, although of not much promise as a magnet material, is interesting from the point of view of superconductivity in layered compounds.[14] These layered compounds consist of two close-packed planes of metalloid, Se in this case, with Nb atoms in between in trigonal prismatic space lattices. The bonding between the Nb and Se atoms within the layers are of the strong covalent type while the bonding between layers are of the weak Van der Waals type. The effect of neutron irradiation on 2H-$NbSe_2$ is shown in Fig. 1 where it is seen that this material is also extremely sensitive to heavy-particle irradiation. For fluences of 3×10^{18} n/cm^2 a reduction in T_c of almost 50% is observed, which may be compared to the A-15's where T_c at the same fluence is decreased only 20%.

The rapid decrease in T_c for 2H-$NbSe_2$ upon irradiation with high-energy neutrons may be understood by noting the sensitivity of T_c to the occupation by Nb atoms of the Nb sub-lattice as shown by Antonova et al.[20] Antonova et al. prepared 2H-$NbSe_2$ with different stoichiometries and T_c was determined as a function of changes in the occupation of the Nb and Se sub-lattice sites as the concentration was varied. A correlation between T_c and the degree of ordering of the Nb sub-lattice was observed suggesting that occupation of the Nb sub-lattice by Nb is important in determining the superconducting properties. The depressions in T_c observed by Antonova et al., from ~6 K to 2 K, are similar to what we observe for the neutron-irradiated samples and most likely arise from the same cause, disruption of the Nb sub-lattice. In the case of the experiments of Antonova et al. disorder in the Nb sub-lattice is produced by a change in composition whereas in the present study disorder is brought about by displacement collisions resulting from the high-energy irradiation without compositional changes.

The effect of irradiation on HfV_2, which crystallizes in a cubic C-15 Laves phase ($MgCu_2$-type), is also indicated in Fig. 1. Of all the materials studied to date this is the only one that is relatively radiation resistant. At fluences where the T_c of the A-15's have been depressed about 30%, the T_c of HfV_2 is decreased only 1%. For high fluences, $\sim10^{19}$ n/cm^2, where the T_c of A-15 superconductors are down by approximately 40%, the T_c of HfV_2 is depressed only 10%. A maximum T_c of 10.1 K and H_{c2} of 23 T have been reported in pseudobinary alloys based on HfV_2 and Tachikawa[9] and co-workers have prepared tapes carrying currents as high as 10^5 A/cm^2 at 13 T making the Laves phase interesting materials for magnet conductors. Their resistance to radiation degradation in the high 10^{18} n/cm^2 range make these materials potentially useful as magnet conductors where such high radiation levels might be expected. Although their T_c's at 10^{19} n/cm^2 would be in the range of 9 K as compared to Nb_3Sn of ~11 K at that fluence, the critical currents and fields of the Laves phases would be much higher than those of Nb_3Sn.

For the A-15 compounds recovery of T_c to close to its unirradiated value is possible by annealing at moderate temperatures, ~700-900°C for various periods of time ranging from 20 minutes to 20 hours depending on the compound. This reversibility of T_c has been observed in Nb_3Sn, Nb_3Al, Nb_3Ga and Nb_3Ge.[15,17,18]

Critical Currents (I_c)

Figure 2 shows the effect of neutron irradiation on the I_c of multifilamentary (19-core) Nb_3Sn wires for fluences from 3×10^{17} to

1.8×10^{19} n/cm^2 (E>1.0 MeV) at transverse magnetic fields up to 16 T. All measurements were made at 4.2 K. For doses below 10^{18} n/cm^2 I_c is enhanced over the unirradiated value, the degree of enhancement being greater at higher field values. This behavior is consistent with an interpretation in which the upper critical field $H_{c2}(4.2)$, increases with increasing dose because of the increase in the normal-state resistivity of the Nb_3Sn caused by defects and increasing disorder. The T_c does not change over this range (see Fig. 1) so changes in I_c are not due to changes in T_c for doses up to ~10^{18} n/cm^2. Above 10^{18} n/cm^2, however, the continuing decrease in the order begins to produce substantial reductions in T_c, which effect outweighs that of the increasing normal-state resistivity. Thus, decreases in I_c are produced as T_c is depressed for doses above 10^{18} n/cm^2. H_{c2} also decreases causing the large depressions in I_c observed in this fluence range.

The change in the reduced critical current I_c/I_{co} as a function of fluence for different fields is shown in Fig. 3. One expects the enhancement to increase in such a plot as the applied field approaches the upper critical field of the unirradiated Nb_3Sn which by extrapolation would lie at ~17 T, and indeed this is what is observed. The peak in the enhancement occurs at a dose of 5×10^{17} n/cm^2 with H_{c2} and I_c decreasing from that dose on. One speculates, then, that at this dose of 5×10^{17} n/cm^2 the tendency to increase H_{c2} caused by the increasing normal-state resistivity is balanced by the tendency to decrease H_{c2} owing to a decreasing T_c. Above 5×10^{17} n/cm^2 the rapidly decreasing T_c thus dominates, causing I_c to rapidly degrade.

These data are interesting to compare to low-temperature irradiations on similar material. Brown et al.[21] irradiated identical multifilamentary Nb_3Sn to fluences of 1.8×10^{18} n/cm^2 at 6 K (to compare fluences from the Argonne reactor with the Brookhaven reactor divide the Argonne fluences by ~3). They found increases in J_c of ~32% relative to the unirradiated value at a field of 3.32 T for an equivalent fluence of 3×10^{17} n/cm^2. The fluence range where the maximum increases are found are close to our ambient temperature results and the magnitude of the increase is of the same order of magnitude.

It should be noted that the Nb_3Sn multifilament wire used in this work was fabricated so as to maximize the critical current density and thus I_c. Many experiments have shown that for Nb_3Sn that is not so optimized, increases in I_c with irradiation are produced, the size of the increases increasing with the lowering of the initial J_c. Our initial value of H_{c2}, ~17 T, is not of the best that can be obtained for Nb_3Sn, ~20 T. It would be instructive to repeat these kinds of measurements with higher initial values of H_{c2} to determine if further enhancement of H_{c2} could be achieved. The ramifications for I_c in this case would also be of interest. The interactions between these critical properties may be an important factor in tailoring metallurgically the best possible A-15 superconductor to use in a fusion reactor where levels to 10^{18} n/cm^2 over a 10-year lifetime might be expected.

CONCLUSIONS

The effect of the radiation field on the superconductor in a magnet used in a CTR device will not present a serious problem with respect to deterioration of the superconducting properties provided the fluence is below ~10^{18} n/cm^2 (E>1 MeV). Below this fluence no significant deterioration in T_c is observed for the A-15 compounds and for Nb_3Sn increases in J_c have been observed. Above this fluence as far as the A-15 compounds are concerned severe degradation takes place both in T_c and J_c making these materials unsuitable for magnet conductors in such high radiation fields. It is possible to restore the superconducting properties by annealing in the 700°C range, but this may not be practical in a working reactor. If such high fluences are to be expected, the Laves phases $(Hf,Zr)V_2$ may be an appropriate material to consider as an alternative to the A-15 compounds. A more serious problem than the superconductor appears to be the normal metal used for stabilization, as discussed in the previous paper.[1]

It is also interesting to compare results of ambient-temperature irradiations (70-150°C) with low-temperature irradiations (6-30 K). With respect to T_c there is very little difference in the depression of T_c for Nb_3Sn whether irradiated at low temperatures or at ambient temperatures.[1,19] The critical-current increases observed for Nb_3Sn when irradiated at low temperatures and low fluence have now also been seen in the ambient temperature irradiations (Fig. 3). Where comparable data exist the effect on I_c for low-temperature and ambient-temperature irradiation are similar.

In order to obtain an understanding of the performance for the complete magnet (superconductor, stabilizer, insulator) low temperature irradiations of the component assembly will be necessary. However, as far as the superconductor is concerned the effects of low-temperature and ambient-temperature irradiations are similar. This means that with respect to the behavior of the superconductor, one can gain meaningful results by irradiation at ambient temperatures.

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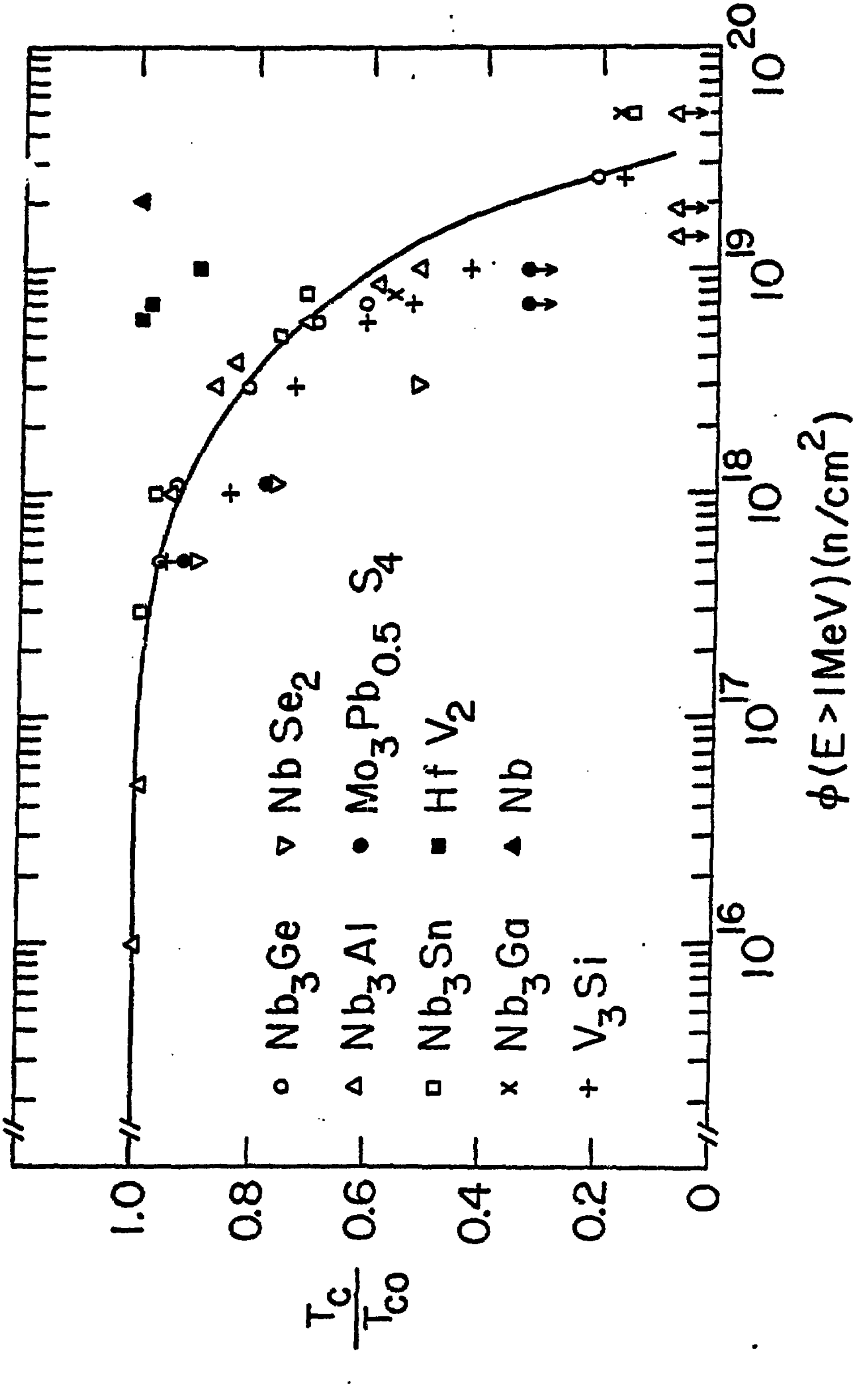
FIGURE LIST

Caption

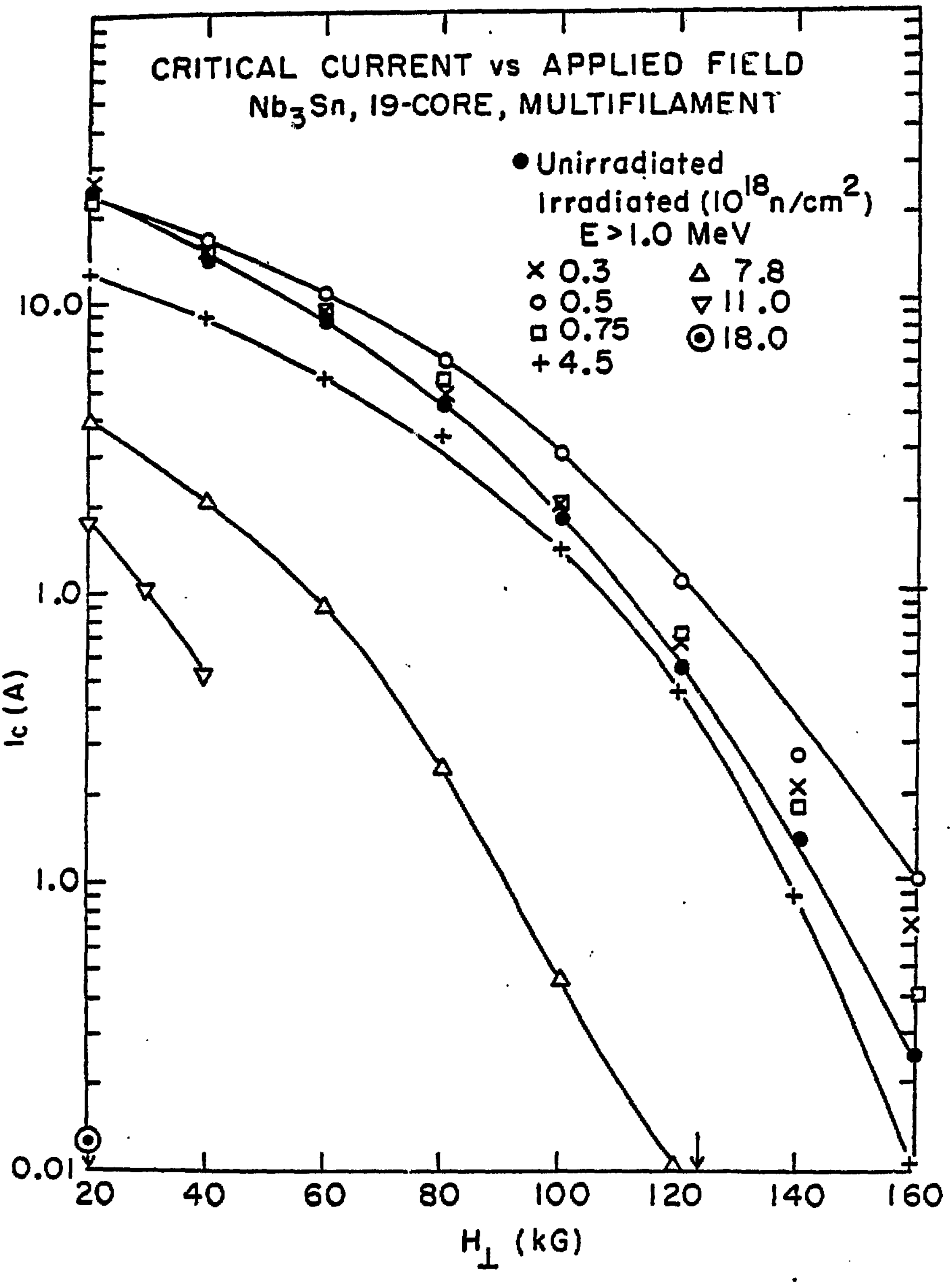
Fig. 1. Reduced transition temperature T_c/T_{co} as a function of high energy neutron (E>1 MeV) fluence for different superconducting compounds. T_c is the transition temperature after irradiation and T_{co} is the value before irradiation. Values of T_{co} are found in Table 1. Curve is drawn as a visual aide. Arrows indicate no superconductivity observed to the indicated temperature.

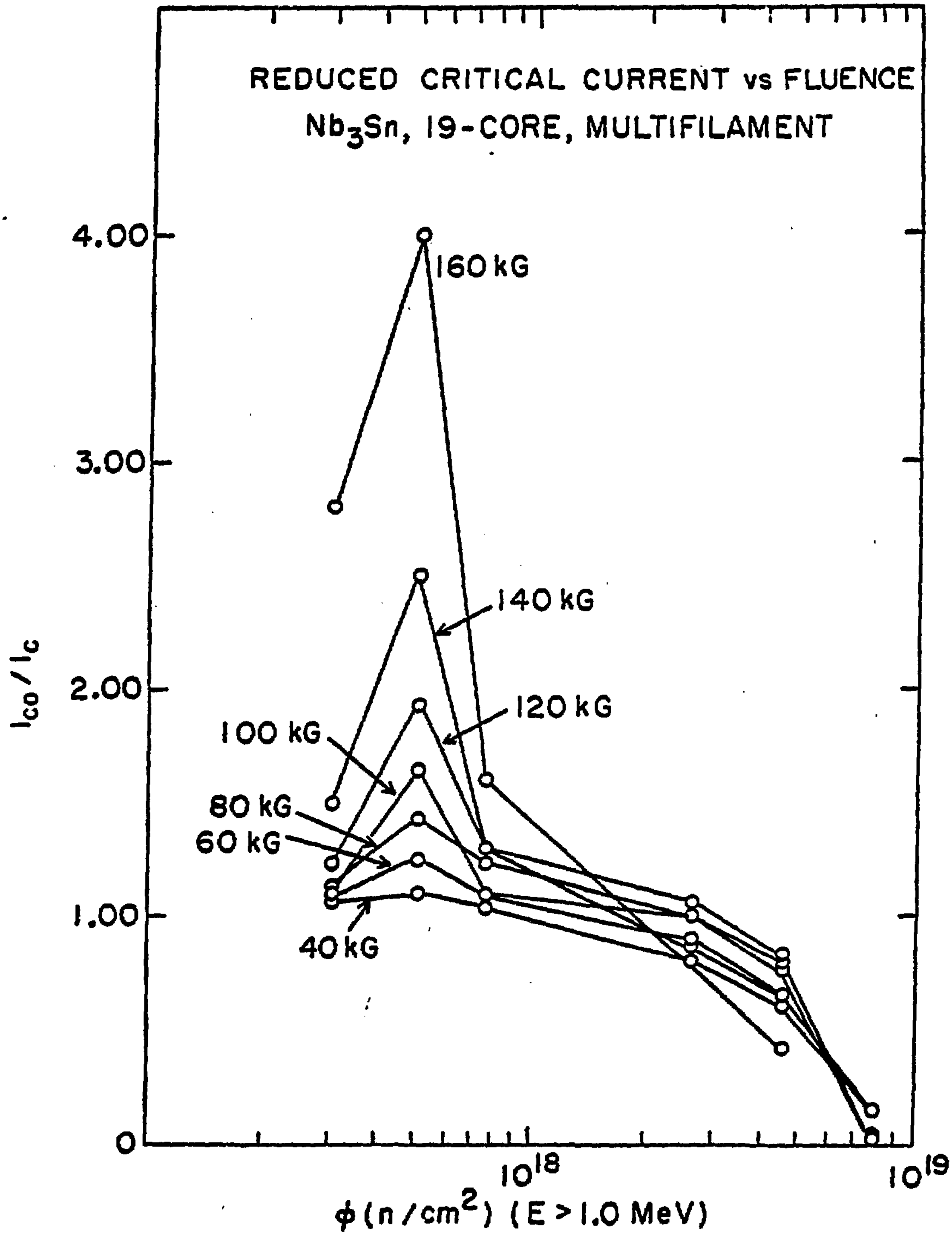
Fig. 2. Critical current I_c vs applied transverse magnetic field H for 19 core multifilamentary Nb_3Sn wire for different fluences. Unirradiated value of $J_c = 10^6$ A/cm^2 at 4 T. To convert I_c to current density divide by 1.5×10^{-5} cm^2.

Fig. 3. Reduced critical current I_c/I_{co} as a function of fluence at different fields for 19 core multifilamentary Nb_3Sn wire.



$\frac{T_c}{T_{co}}$
1.0
0.8
0.6
0.4
0.2
0
10^{16}
10^{17}
10^{18}
10^{19}
10^{20}
$\phi(E > 1 MeV)(n/cm^2)$
○ Nb_3Ge
△ Nb_3Al
□ Nb_3Sn
× Nb_3Ga
+ V_3Si
▽ $NbSe_2$
● $Mo_3Pb_{0.5}S_4$
■ HfV_2
▲ Nb


CRITICAL CURRENT vs APPLIED FIELD
Nb_3Sn, 19-CORE, MULTIFILAMENT
● Unirradiated
Irradiated (10^{18} n/cm^2)
E>1.0 MeV
× 0.3
○ 0.5
□ 0.75
+ 4.5
△ 7.8
▽ 11.0
◉ 18.0
10.0
1.0
1.0
0.01
I_c (A)
20
40
60
80
100
120
140
160
$H_\perp$ (kG)


REDUCED CRITICAL CURRENT vs FLUENCE
Nb_3Sn, 19-CORE, MULTIFILAMENT
4.00
3.00
2.00
1.00
0
I_{co}/I_c
160 kG
140 kG
120 kG
100 kG
80 kG
60 kG
40 kG
10^{18}
10^{19}
ϕ (n/cm^2) (E > 1.0 MeV)