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Superconducting Materials for Large Scale Applications*

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Introduction

The main reason for the application of superconductivity to large scale electrical devices is that superconductors are capable of handling extremely large current densities. The normally allowed maximum rating of uncooled copper is 2×10^6 A/m^2. This can be increased by forced cooling though the need for passages through which the coolant can flow reduces the overall current density to a value which is usually less than 10^8 A/m^2. Superconductors are capable of carrying current densities of 10^9-10^{11} A/m^2 in the conductor itself, reduced to 10^8-10^{10} A/m^2 overall, because of the need for stability and mechanical reinforcement. These high current densities allow of the construction of smaller, lighter and more compact machines, and it is largely this reduction in size which makes a superconducting machine attractive, lowering both capital and running costs. The reduced power requirements for large superconducting magnets are also an important consideration.

The principal requirement of the superconductor is that it

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should have as high as possible a critical current density, J_c. This is supplemented by other requirements. The superconductor normally operates in a high field environment, and a high value of the upper critical field H_{c2} is desirable. Because the cost of refrigeration, for a given load, varies inversely with temperature, it is useful to be able to operate the device at as high a temperature as possible. This requires that the superconductor has a high critical temperature, T_c; also advantageous as J_c and H_{c2} to some extent scale with T_c. T_c and H_{c2} are intrinsic properties of the superconductor. If the conductor is to see alternating current, or ripple fields, then low ac losses are a requirement. Losses can be reduced by appropriate metallurgical treatment. It must be possible to fabricate the conductor in long (>1 km) lengths. The conductor must also be stable against flux jumps, and sudden changes in current, field or temperature. This requires that the superconductor be small in at least one dimension, that parallel to the direction of flux motion, and be associated with good, normal conductor (copper or aluminum). A multifilamentary configuration is most effective in promoting stability. The cost should be low, the availability of the constituents good, and in the case of materials for CTR magnets, resistance to irradiation is an asset, as this will reduce the need to shield magnet windings from the neutron flux.

Critical Current Density

The ultimate current density that a superconductor is capable of carrying is that in which the kinetic energy of the electrons is equal to the superconducting condensation energy. This is known as the depairing current and is estimated to be 10^{12}-10^{13} A/m^2. This current density is never achieved in practice. Measured values of J_c are determined by the pinning of flux vortices by microstructural inhomogeneities. When the Lorentz force (JxB) exceeds the maximum pinning force (F_p) flux lines begin to move across the conductor and an emf is generated.(1) J_c is thus not, unlike T_c and H_{c2}, an intrinsic property of a particular alloy or compound, but is strongly influenced by the microstructure of the actual specimen. Within limits J_c can be controlled by metallurgical techniques such as precipitation, cold-work and low temperature annealing.(2) The ultimate current density can be limited by the mechanical strength of the conductor. The Lorentz force must not exceed the flow or fracture stress of the material.(3) Many conductor designs include added mechanical reinforcement.

Superconducting Materials Currently Available

Properties of superconductors currently available from commercial sources are summarized in Table I.

Ductile materials can be produced by conventional wire-drawing techniques. Niobium-titanium is generally superior to niobium-zirconium both in terms of its superconducting properties and fabrication behavior. It can be produced in a variety of configurations to meet the demands of the device builder in terms of high overall J_c and stability. Multifilamentary material, in both copper and aluminum matrices, is readily fabricated. Filaments can be decoupled by the use of a highly-resistive barrier such as cupro-nickel. Examples shown in Figs. 1-3 respectively are 241 filaments of Nb-Ti, each surrounded by Cu and then by cupro-nickel,(4) 1045 filaments of Nb-Ti, each surrounded by cupro-nickel in a Cu matrix,(4) and 13,255 filaments of Nb-Ti in a Cu matrix, decoupled by cupro-nickel barriers.(5)

The brittle A-15 compounds Nb_3Sn and V_3Ga are formed as tapes by chemical vapor deposition (CVD) on a suitable substrate, or by reaction of Nb(V) tapes with molten Sn(Ga). Stabilization is provided by cladding with copper, strength by cladding with stainless steel. Multifilamentary material is produced by the bronze process. Filaments of Nb(V) are drawn down in a matrix of Sn(Ga)-Cu alloy (bronze); subsequent heat-treatment allows of the formation of Nb_3Sn (V_3Ga) by reaction between the filaments and the Sn(Ga) in the matrix. The matrix contains residual Sn(Ga) and is too resistive for proper stabilization. Copper can be incorporated if protected from the matrix by an inert diffusion barrier.(6) Examples shown in Figs. 4 and 5 are of 41,070 filaments of Nb_3Sn, with incorporated Cu filaments,(7) and 67,507 filaments of Nb_3Sn, each group of filaments in a bronze matrix separated by a tantalum barrier from the pure Cu matrix of the entire conductor.(8) Figure 6 shows a V_3Ga conductor which has six 55 filament strands cabled on a tungsten center-wire for strength; the cable is impregnated with indium.(9)

Conductors are twisted to allow of rapid rise-times, and for pulsed applications.

The cost of conductors, expressed in terms of the quantity required to produce a field of given strength and volume, is shown in Fig. 7. The figures are not recent, their absolute value may have changed, but the relative positions of the different conductors is probably similar. Revising the prices is difficult as manufacturers will only quote for specific orders. Nb-Ti is least expensive for fields below 10 tesla, but ceases to carry significant current above this field. Nb_3Sn therefore takes over for high-field devices. However, due to its high current density at very high fields, V_3Ga appears to be cheaper than Nb_3Sn above about 12 tesla. This point is not quite clear as the only commercial V_3Ga

is produced in Japan, the quoted price may not be realistic, and the crossover point could occur at higher fields.

ac losses are summarized in Fig. 8. The measured Nb_3Sn samples range from commercial materials produced with no attempt to reduce losses, to experimental material in which low losses are of prime importance. The former lie within a factor of 10 of the maximum acceptable losses for the BNL cable study. The latter, achieved by control of surface roughness, lie well below the minimum requirements.(10) Nb_3Sn is suitable for use in power cables, where the dominant losses now originate in components other than the superconductor. Losses in V_3Ga are, to date, too high to consider this material for ac applications. At 4.2 K pure Nb is better than Nb_3Sn, at low surface current densities, but the latter gains an advantage as the temperature or surface current density is raised.

Alloys, such as NbTi, are not particularly susceptible to radiation damage, and in some instances J_c is increased after irradiation. They are therefore suitable for CTR magnets with fields <10 tesla. A-15 compound superconductors irradiated by fast neutrons undergo severe degradation of T_c and other superconducting properties when the fluence exceeds 10^{18} nvt.(11) The use of these materials in CTR magnets will require them to be shielded from the intense neutron flux generated in the reactor.

Future Prospects for Improved Superconducting Materials

The most desirable immediate goal is to increase J_c at high fields. A look at the Lorentz force (JxB) curves versus reduced field $h(=H/H_{c2})$ for A-15 compounds shows a general trend (Fig. 9). As J_c increases, the peak in the Lorentz force moves to lower values of h, With the exception of V_3Ga, the curves for all materials fall within a single envelope. When the results for V_3Ga are plotted in terms of its true H_{c2}, (33 tesla), rather than the experimentally observed, strongly paramagnetically limited value (22 tesla) they too can be seen to conform to the general pattern. It is concluded that to get a high J_c at high fields it is necessary to go to a material which has a high H_{c2}. The prospect of producing a significant increase in T_c in known materials is not thought to be good; attempts at manipulating materials are more likely to lower T_c.

Materials with high values of H_{c2} are summarized in Table II; H_{c2} versus T curves are shown in Fig. 10.

The A-15 compounds listed all have values of T_c and H_{c2} superior to those for Nb_3Sn, and should therefore provide improved performance. Nb_3Al conductor has been produced by solid state diffusion, but with inferior properties. Nb_3Ga has not been successfully produced as a conductor. Neither of these materials has intrinsic properties which make them more attractive then Nb_3Ge or $Nb_3(Al,Ge)$, both of which have been produced as flexible conductor. Nb_3Ge tapes produced by CVD have T_c close to 23 K, though critical current density is inferior to that of Nb_3Sn at 4.2 K.(12) This material is to be preferred where superior performance at high temperatures (11-12 K) is required. J_c at high fields should be maximized in $Nb_3(Al,Ge)$. Conductor of this material has been produced by high rate sputtering.(13) These two compounds (Nb_3Ge and $Nb_3(Al,Ge)$) represent the most fruitful immediate avenue for the development of new commercial superconductors.

The only class of bulk materials in which H_{c2} is higher than for A-15 compounds is the ternary lead molybdenum sulphides, of which the optimum composition appears to be $PbMo_{5.1}S_6$. This compound has T_c of 14.6 K and H_{c2} (4.2 K) = 50 tesla.(14) Preliminary experiments at BNL have shown that wire can be produced by sintering powder drawn down in tubes of a suitable material.(15) Current densities to date are poor (some hundred times less than those available in Nb_3Sn) but improvements are possible. This material does seem to be even more sensitive to mechanical and radiation damage than are the A-15 compounds. However it should not be written off at this early stage in its development.

The final class of known materials with potential for development into commercial conductors is the C15 (Laves phase) compounds, based on V_2Hf. If some of the Hf is replaced by Zr T_c can be raised to 10 K, and H_{c2} to 24 tesla. An isomorphous compound, $(V,Nb)_2Hf$ has T_c=10.4 K and H_{c2}~26 tesla.(16) These compounds thus have critical temperatures slightly higher than that for Nb-Ti, and upper critical fields equal, or superior, to that for Nb_3Sn. Unlike the A-15 compounds, they are thought to have some ductility, and could be hot-worked. They have an additional advantage over the A-15s in that they are not so sensitive to radiation damage.(17) Tapes and multifilamentary conductors can be produced by solid state diffusion. These materials have potential for high field CTR magnets. No other presently known superconductors appear to have commercial possibilities.

The probability of finding new superconductors with higher critical temperatures (and hence higher H_{c2} and J_c) is not thought to be good. The compromise between metallic and covalent bonding that is now believed to be desirable for high critical temperatures is probably optimized in the A-15 structure(18) with a maximum T_c~23 K.(19) The search for new mechanisms for superconductivity has so far proved unsuccessful.

Table I

Commercial Superconducting Materials
Currently Available

Material	T_c(K)	H_{c2}(T) at 4.2 K	J_c(10^5 am/cm^2) at 4.2 K 2.5T	5T	10T	15T	Fabrication
Nb-25 wt.% Zr	11	7.0	1.1	0.8	0	0	Fairly Ductile
Nb-33 wt.% Zr	11.5	8.0	0.9	0.8	0	0	Fairly Ductile
Nb-48 wt.% Ti	9.5	12.0	2.5	1.5	0.3	0	Ductile
Nb_3Sn	18.0	22.0	17.0	10.0	4.0	0.5	CVD Diffusion Bronze
V_3Ga	15.0	23.0	5.0	2.5	1.4	0.9	Diffusion Bronze

Average Values from Manufacturer's Data

Table II

Superconducting Materials

Future Prospects

Material A15	T_c(K)	H_{c2}(T) at 4.2 K	Fabrication
Nb_3Al	18.9	30	Diffusion (poor)
Nb_3Ga	20.3	33	?
Nb_3Ge	22.5	37	CVD
$Nb_3(Al,Ge)$	21.0	41	Sputtering
Ternary Sulphides			
$PbMo_{5.1}S_6$	14.6	50	Powder Metallurgy
C_{15} (Laves Phase)			
$V_2(Hf,Zr)$	10	24	Diffusion
$(V,Nb)_2Hf$	10.4	26	Diffusion

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Figure Captions

Figure 1. Commercial multifilamentary Nb-Ti wire composite; each of the 241 Nb-Ti filaments surrounded by copper and then by cupro-nickel (1.M.1., ref. 4).

Figure 2. 1045 filament conductor; each Nb-Ti filament is surrounded by cupronickel and then by copper (1.M.1., ref. 4).

Figure 3. 13,255 filament conductor for pulsed magnet applications. Groups of 241 Nb-Ti filaments, sheathed in copper and cupronickel as in figure 1, are packed in a copper matrix, and separated from neighboring groups by cupronickel barriers (ref. 5).

Figure 4. Multifilamentary Nb_3 Sn conductor fabricated by the bronze process. 41,070 filaments of Nb_3 Sn are contained in a tin bronze matrix. Pure copper, for stabilization, is seperated from the bronze by a diffusion barrier (UKAEA Harwell, ref. 7).

Figure 5. An alternative approach to stabilized multifilamentary Nb_3 Sn conductor. Groups of filaments in a bronze matrix are seperated, by a tantalum diffusion barrier, from the overall copper matrix. The total number of filaments is 67,507. (Airco, ref. 8).

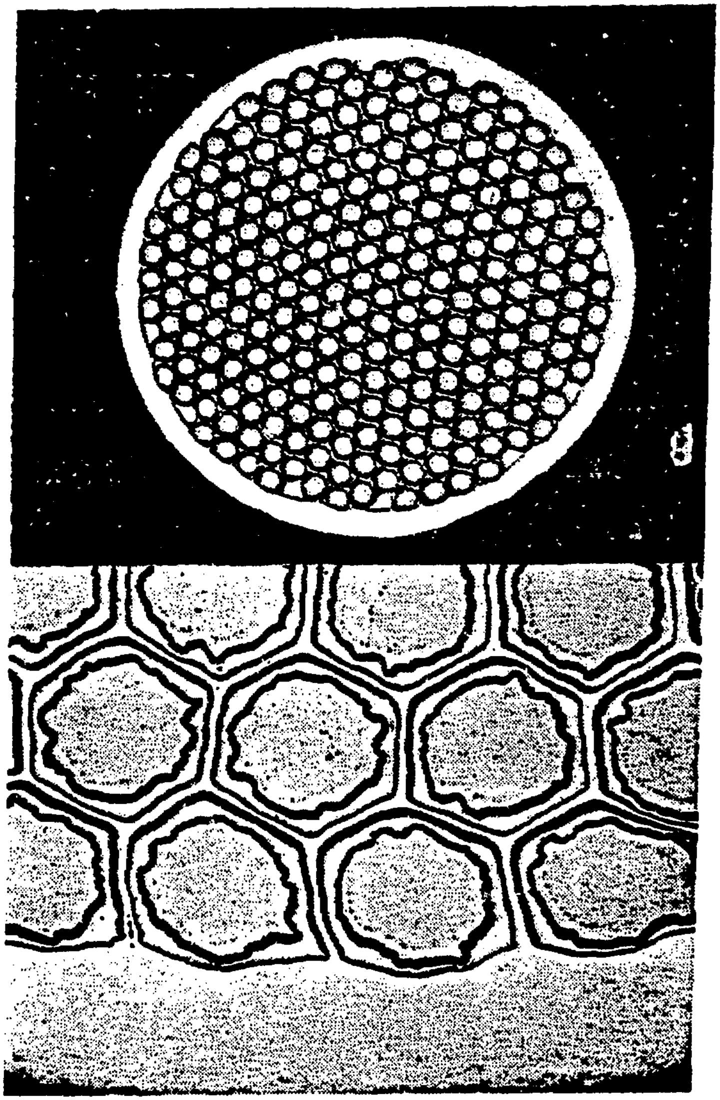
Figure 6 330 filament V_3 Ga conductor. 6 strands of gallium bronze each containing 55 filaments of V_3 ga are twisted around a central supporting strand of tungsten. Bonding and stabilization is provided by impregnating the resultant cable with indium.

Figure 7 Relative costs of various conductor materials, expressed in pounds sterling per cm. per kiloamp, as a function of the magnetic field in which they are to perform. Data supplied by P. Hanley (ref. 3).

Figure 8 ac losses in superconductors. The data for V_3 Ga are averaged from measurements on several samples. The band for Nb_3 Sn represents data from commercial magnet conductor, from various sources, fabricated with no intention of minimizing losses, to the best laboratory samples in which low losses have been the primary objective. The band for pure irrobium is an average of the best data for that material. Data supplied by J. F. Bussiere.

Figure 9 Lorentz Force, J_c x B, for various A15 compound conductors, versus the reduced field h (= H/H_{c2}). (See reference 19 for sources of original data).

Figure 10 Upper critical field, H_{c2} versus temperature for various superconducting compounds. (Data on $Pb\ Mo_{5.1}\ S_6$ from reference 14, on C15 compounds interpolated from reference 16, sources of data for A15 compounds given in reference 19).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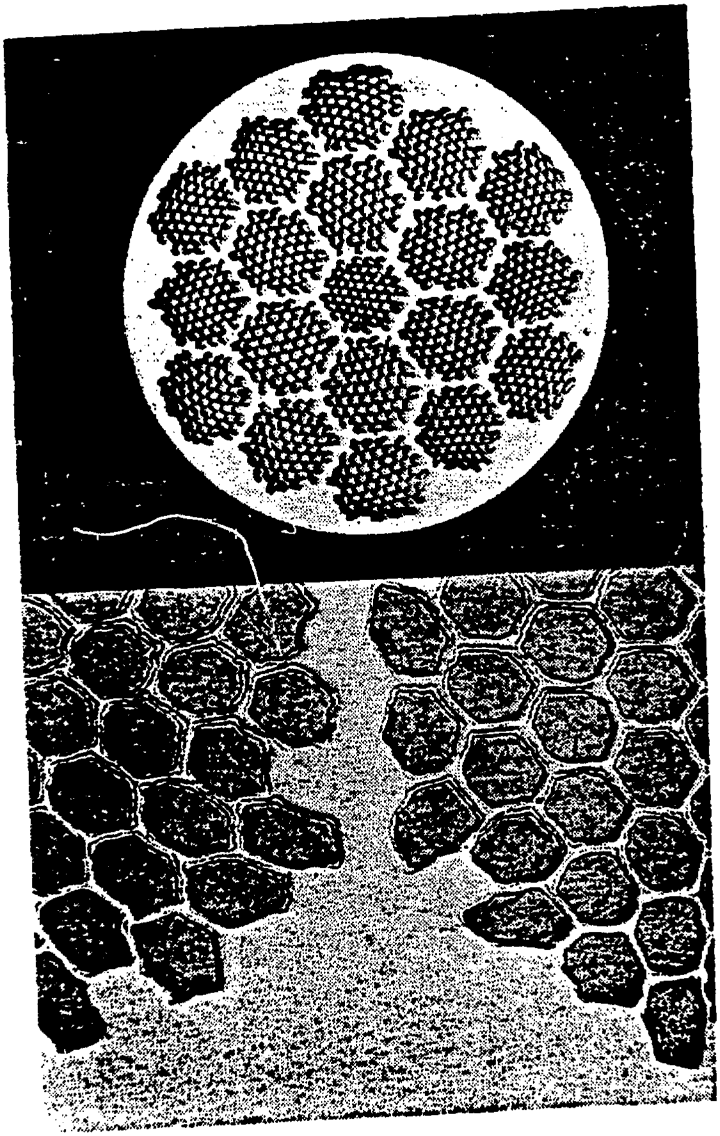

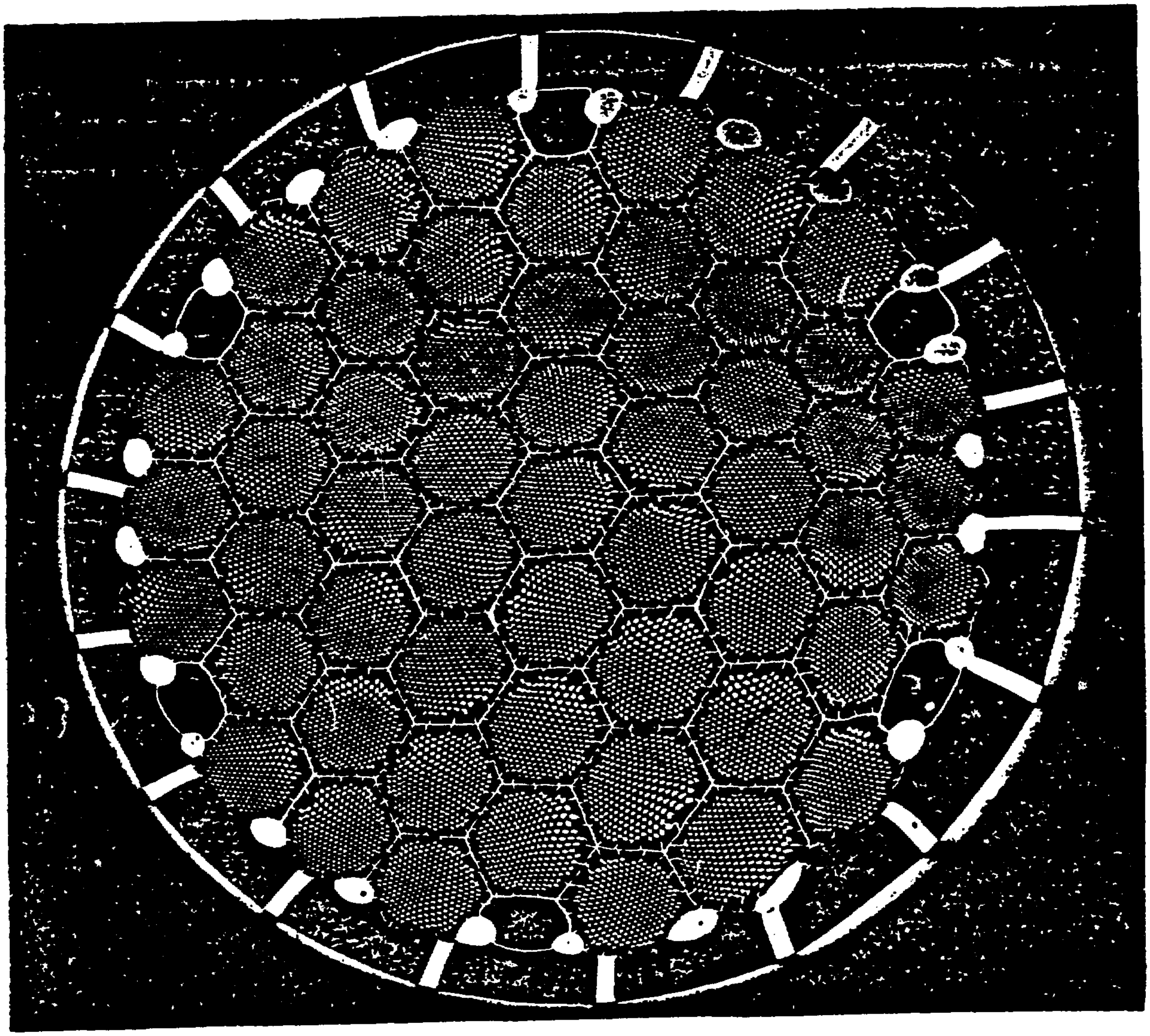

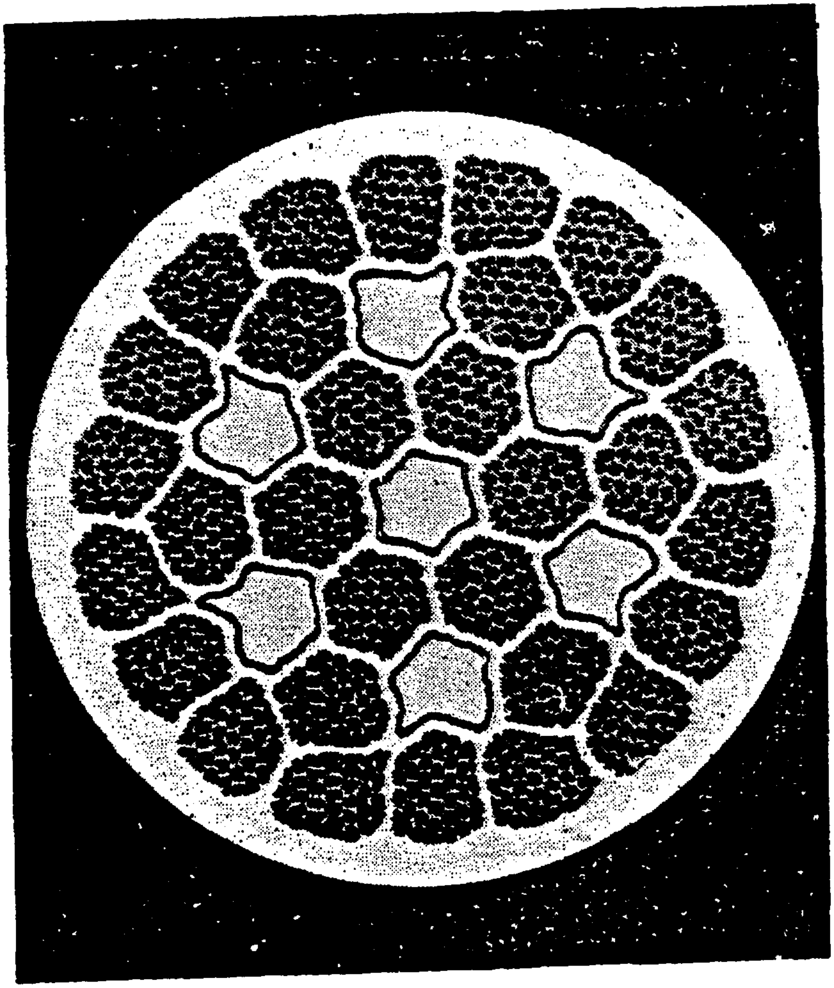

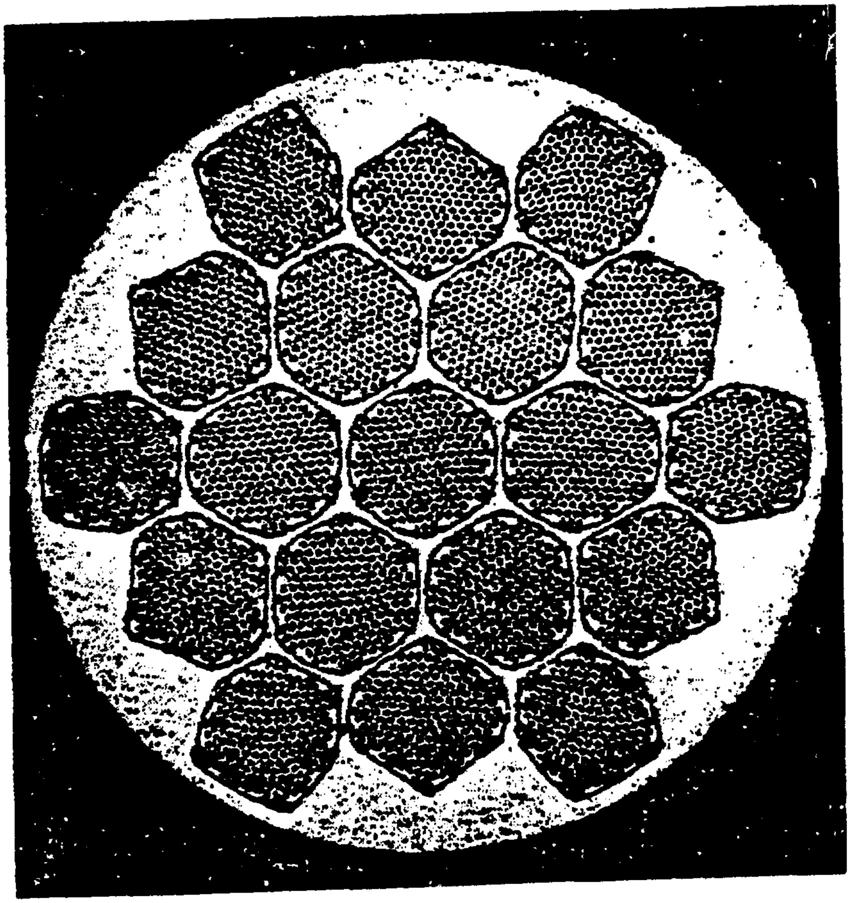

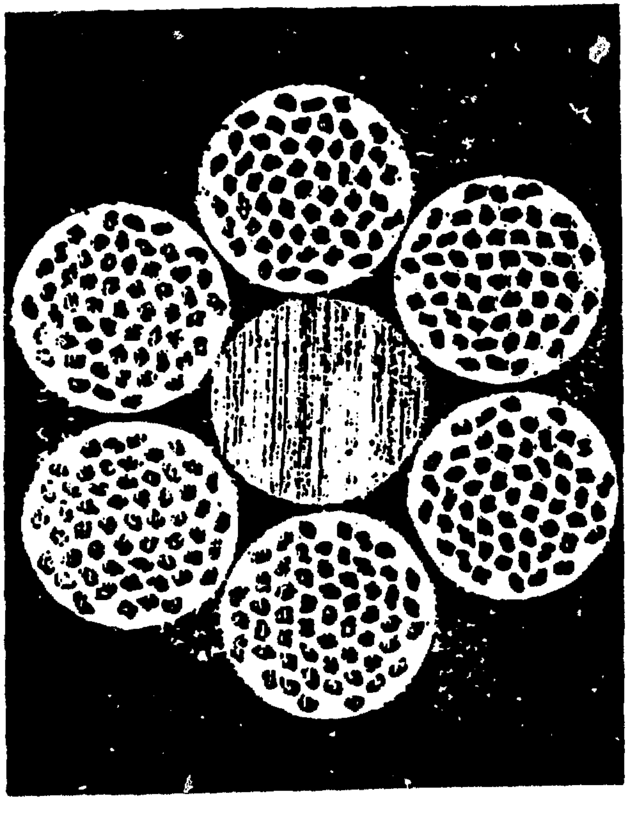

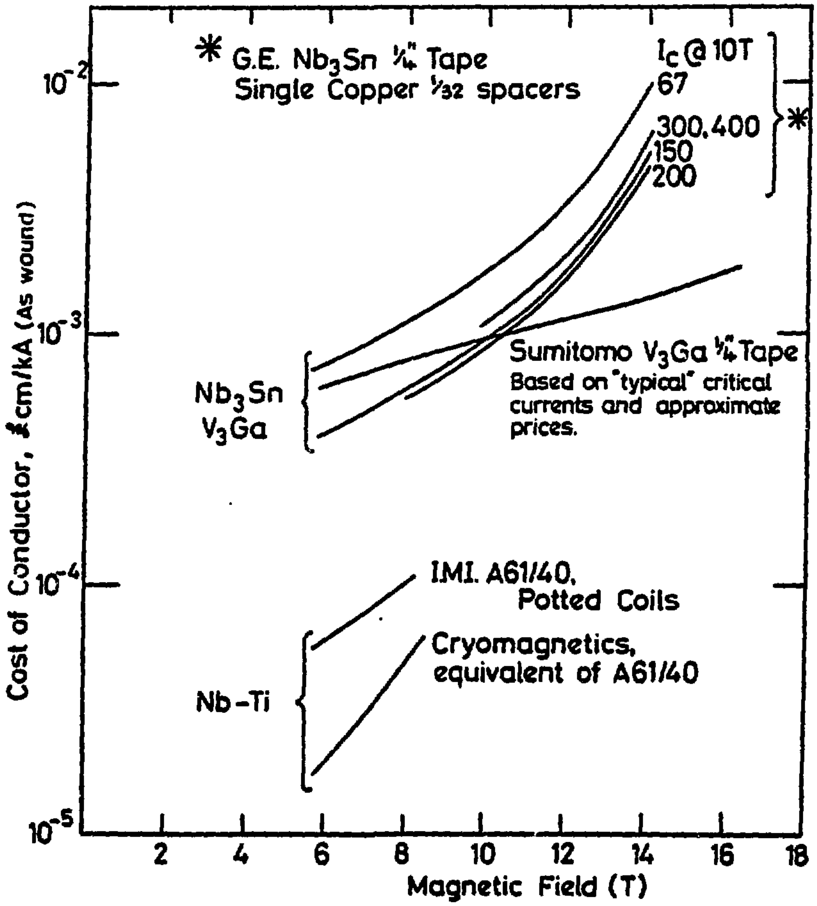

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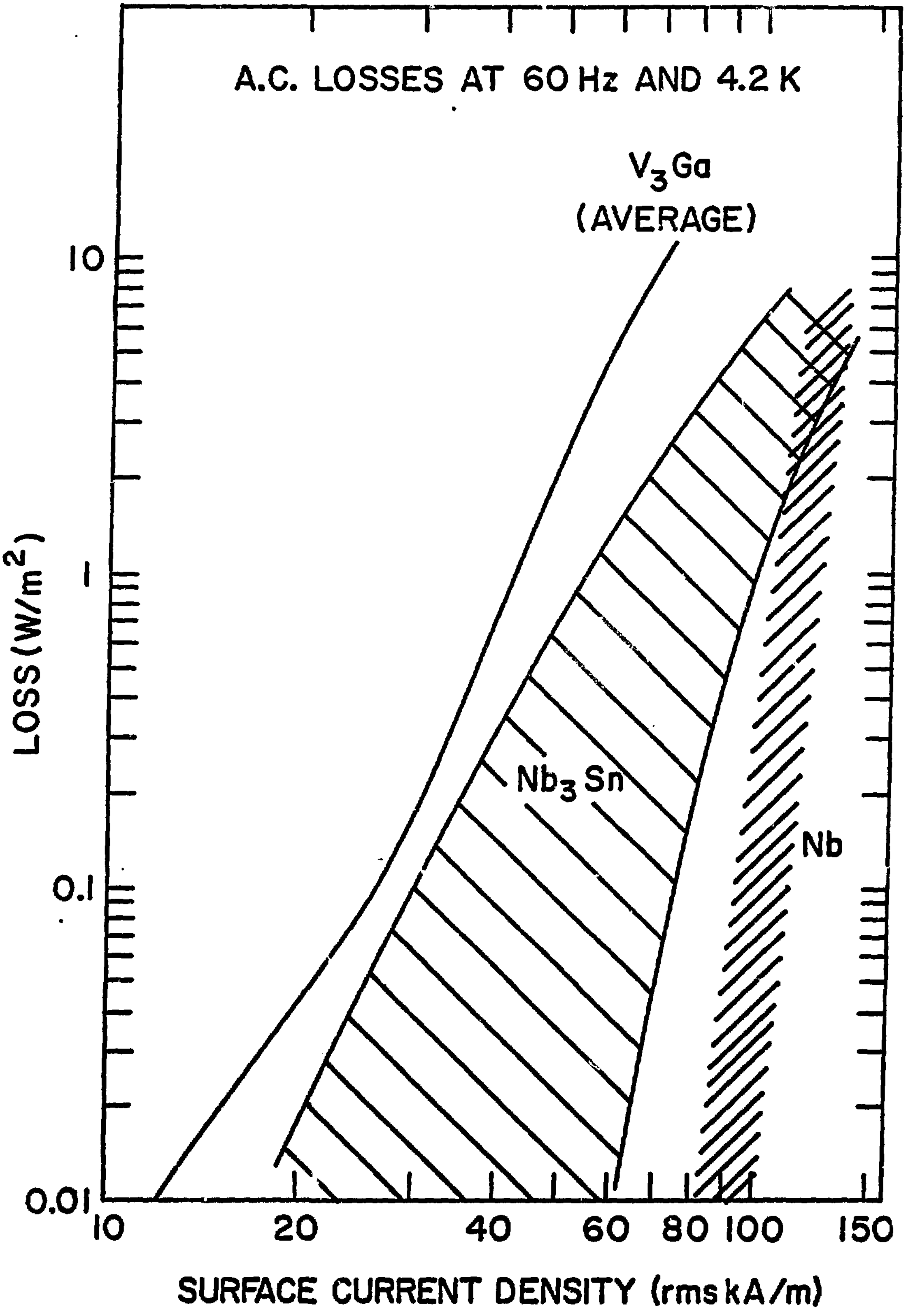
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Nb_3Sn
Nb
LOSS (W/m^2)
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0.01
10
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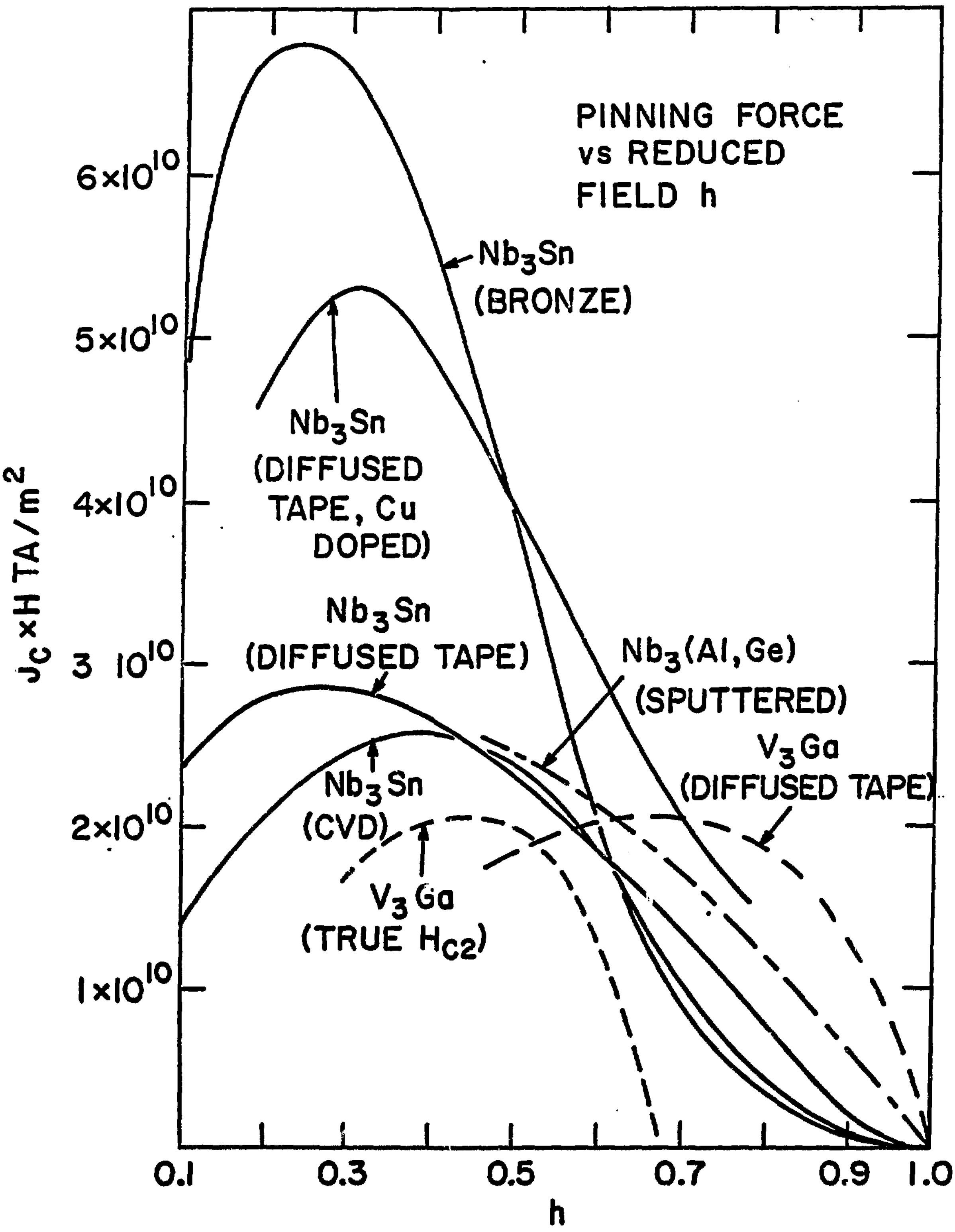
40
60
80
100
150
SURFACE CURRENT DENSITY (rms kA/m)


PINNING FORCE
vs REDUCED
FIELD h
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5×10^{10}
4×10^{10}
3 10^{10}
2×10^{10}
1×10^{10}
Nb$_3$Sn (BRONZE)
Nb$_3$Sn (DIFFUSED TAPE, Cu DOPED)
Nb$_3$Sn (DIFFUSED TAPE)
Nb$_3$(Al, Ge) (SPUTTERED)
V$_3$Ga (DIFFUSED TAPE)
Nb$_3$Sn (CVD)
V$_3$Ga (TRUE H$_{C2}$)
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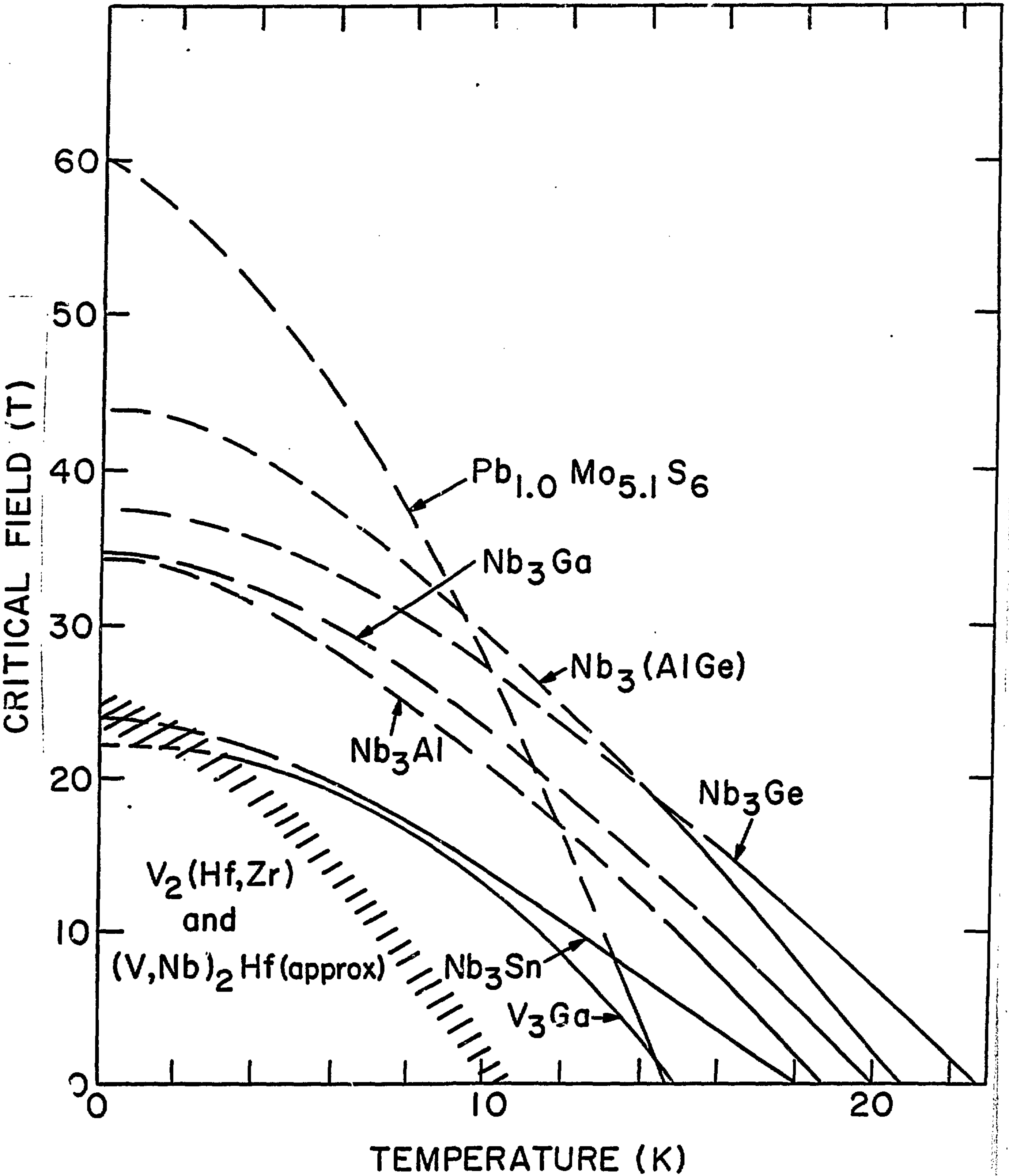
0.9
1.0
h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Nb_3Ga
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Nb_3Al
Nb_3Ge
$V_2(Hf,Zr)$
and
$(V,Nb)_2Hf$ (approx)
Nb_3Sn
V_3Ga