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Comments on Defect Production and Stoichiometry in A-15 Superconductors

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(Received 10 June 1976)

The dependence of T_c upon 2-MeV ^{4}He damage has been investigated in Nb_3Ge, Nb_3Sn, V_3Si, and V_3Ge superconducting thin films. Similar T_c versus dose plots are observed for all materials. At high doses T_c saturates at 3.5 K (Nb_3Ge), 2.95 K (Nb_3Sn), 2.2 K (V_3Si), and 1.0 K (V_3Ge). Optimum values of T_c are obtained for Nb:Ge and Nb:Sn ratios throughout the compositional range of 2.6:1–3:1 in 95% single-phase A15 films.

Superconductivity in the A15 materials is a subject of continuing interest with the crucial question being what determines or limits the superconducting transition temperature T_c. There have been several recent Letters[1,2] and publications[3,4] which address various aspects of this problem. Sweedler, Schweitzer, and Webb[1] were the first to show a universal behavior of T_c versus neutron damage curves for the A15 materials. They correlated the density of antisite (or antistructure) defects (i.e., interchange of A and B sites) with degradation in T_c. For example, in their analysis[3] of Nb_3Al when 7.3% of the Nb chains were occupied by Al atoms, T_c was degraded from 18.6 to 9.6 K.

We had previously examined the Nb_3Ge system in detail with regard to stoichiometry versus T_c and ^{4}He damage versus T_c dependences.[2,4] Significant differences emerged from our results and those of the Brookhaven National Laboratory group. It did not appear that simple antistructure defects were solely the culpable defects with regard to T_c degradation as stoichiometries could be varied so that 5% of the Nb chains were occupied by Ge while maintaining $T_c \sim 20$ K. While the general features of the ^{4}He and neutron damage curves agreed well, there were two significant differences. Firstly, ^{4}He damage in Nb_3Ge produced a saturated region in T_c after high doses at $T_c \sim 3.5$ K and this did not degrade with increasing dose; the neutrons appeared to depress T_c below 1.5 K with no saturation region.[5] Secondly, the transition widths in the intermediate region, where T_c was rapidly degrading with dose, were found to increase significantly for ^{4}He damage but not for neutron damage.

In this communication we briefly report extensions of our measurements into the following A15 materials: Nb_3Ge, Nb_3Sn, V_3Si, and V_3Ge. The motivation was to determine trends and to establish whether the Nb-Ge results were pathological or indeed representative of universal behavior in the A15 materials. Ion-beam and x-ray diffraction techniques[2,4] were used to analyze the films and to induce defects. The V_3Si and V_3Ge films were prepared, in the dc getter-sputtering system described previously[4] with composition ratios of 3:1. The majority of the Nb_3Sn films were produced at Stanford University using the dual-electron-beam codeposition technique.[6] Films of varying composition were produced by this technique. All films, whether sputter or e-beam produced, were deposited on clean sapphire substrates held at temperatures typically in the range 700–800°C. Film thicknesses were in the range 2000–3000 Å.

Standard four-probe resistance measurements were made using pressure, silver paste, or soldered contacts. Temperatures were measured to an accuracy of ± 0.2 K with calibrated carbon and germanium resistors and/or silicon diodes. T_c's below 4 K were determined by pumping on the ^{4}He in the Dewar and measuring the He vapor pressure (the width of the superconducting transition is taken as 95–5% of the normal state resistance and T_c is the midpoint). For damage production the samples were irradiated with 2-MeV ^{4}He particles at a typical particle density of 3×10^{15} cm^{-2} sec^{-1} (1 μA ^{4}He$^+$ on 2 mm beam-spot size). It should be noted that no ^{4}He lodges in the films but penetrates ~ 5 μm into the sapphire substrates. The beam was swept both vertically and horizontally over a defining collimator of 5.5×5.5 mm^2. It is believed that the integrated dose is constant to within 5% over this area. Sample temperatures rose to no greater than 50°C during irradiations. Irradiations were carried out at pressures of 10^{-7} Torr. X-ray diffraction data were obtained on the films before and after the damage irradiations using either a Read or Seemann-Bohlin camera.

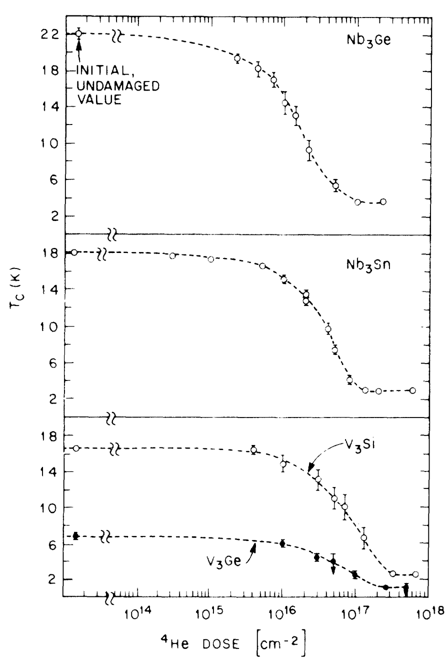

FIG. 1. T_c vs 2-MeV ^{4}He bombardment dose for Nb_3Ge, Nb_3Sn, V_3Si, and V_3Ge. Dashed lines are only meant to guide the eye.

TABLE I. T_c values for initial and final states. Transition widths less than or of the order 1 K.

	T_c (initial) (K)	T_c (saturated) (K)
Nb_3Ge	22	3.5
Nb_3Sn	18.1	2.95
V_3Si	16.8	2.2
V_3Ge	6.5	1.0

The dependence of T_c upon ^{4}He damage for the four sets of $A15$ films is shown in Fig. 1. All films show similar behavior. There is an initial plateau region where T_c is insensitive to low ^{4}He doses; T_c then decreases rapidly for doses in the region 10^{16}–10^{17} cm^{-2}. Beyond this, a saturation region is attained where T_c does not degrade with dose. The 5–95% values of the resistive transitions are plotted except where they are of the order of the size of the data points (midpoints of the transitions). The initial, undamaged T_c values of the films and final saturated values of T_c are shown in Table I. The x-ray diffraction data show that after damage the high-angle lines for all materials became more diffuse in nature and that the lattices expanded. Table II shows the lattice parameter, a_0, of Nb_3Ge, Nb_3Sn, and V_3Si before bombardment and the amount of lattice expansion, $\Delta a/a_0$, when the saturation region has been attained. The relative error in $\Delta a/a_0$ is ~ 30%. The lattice expansion data were not obtained in the V_3Ge case because in the process of etching off the contacts the heavily damaged sample was destroyed.

We will firstly consider the implications of the saturated states and whether they are artifacts of

TABLE II. Lattice parameter expansion following damage to saturation.

	a_0 (Å)	$\Delta a/a_0$ (10^{-3})
Nb_3Ge	5.138	10
Nb_3Sn	5.295	6
V_3Si	4.727	1.7

^{4}He damage as compared to neutron damage. At high ^{4}He doses, T_c saturates as a function of dose for all four compounds with the saturated values given in Table I. This does not necessarily imply that the damage is also saturating as is shown by our x-ray measurements of highly damaged, but initially high-T_c Nb_3Ge and Nb_3Sn films and films that have been deposited on room-temperature substrates. The highly damaged films, while displaying considerable disorder, retain some crystallinity whereas the films deposited at room temperature appear much more disordered. However, the T_c's of the highly damaged or room-temperature-deposited films are identical (3.5 K for Nb_3Ge and 2.9 K for Nb_3Sn). For this reason, and because the transitions are narrow in this saturation region, we believe that we are measuring a bulk property. The fact that our transitions are measured resistively, is then not significant when comparing these results with the inductive measurements of the Brookhaven National Laboratory group. Rowell and Schmidt[7] have performed tunneling measurements successfully on Nb_3Ge. Even in the highest T_c samples, two energy gaps are identified. The larger of these can be associated with well-ordered $A15$ material. The smaller gap correlates extremely well with our highly damaged state (the gap value, $2\Delta_L = 1.0$ meV, giving $T_c \sim 3.3$ K).

It is interesting that the saturated T_c states, whether produced by bombardment or nonoptimum deposition, have identical T_c's even though the crystallinity of the films can be very different. This probably indicates that once a sufficient degree of disorder has been introduced, T_c will degrade no further. Similar highly disordered states for transition metals and transition-metal alloys have been produced by evaporation onto substrates cooled to liquid-helium temperatures.[8] The question still remains as to why the neutron damage apparently reduces T_c below the limiting values of these highly disordered states. As has been discussed[2,10] previously, the morphology of damage resulting from ^{4}He or neutron irradiation should be somewhat different. However, the observation that the depression of T_c to half in maximum value occurs for approximately the same equivalent doses[2] leads us to believe that there are no gross differences between ^{4}He or neutron irradiations.

The damage curves of Fig. 1 show that all four $A15$'s display approximately the same variations in superconducting transition widths as a function of ^{4}He dose. The transition widths are very narrow in the undamaged and saturated states. In the intermediate region, however, where T_c is decreasing rapidly with dose, the widths increase quite markedly. This does not appear to be due to experimental artifacts or an intrinsic property of the film, but rather a reproducible physical effect. The widths indicate inhomogeneities in the films on the scale of the coherence length (~ 50–100 Å), but these inhomogeneities cannot be due to gross changes in composition on that scale (^{4}He damage produces no compositional changes other than minor microscopic rearrangements due to the collision cascade, for example). Instead, it would seem that there are inhomogeneities in the damage densities throughout the films. This can be pictured in terms of the individual collision cascade regions. When the density of cascades is low, there will be an uneven spatial distribution throughout the film due to the statistical nature of the process. At high cascade densities, the statistics improve and damage will be more evenly distributed.

Although the T_c vs ^{4}He dose curves have similar shapes, there are obvious differences in the sensitivity to damage. For example, the doses required to reduce T_c to 50% of the initial undamaged values are 2×10^{16} cm^{-2} (Nb_3Ge), 5×10^{16} (Nb_3Sn), and 10^{17} (V_3Si). This sensitivity to damage probably reflects the intrinsic structural stability of the materials, with Nb_3Ge being the most unstable.

In our earlier studies[4] of Nb-Ge films we demonstrated that T_c was rather insensitive to composition changes for essentially single-phase material. Even at Nb:Ge composition ratios of 4:1 a T_c of 12 K was obtained. The present studies of the Nb-Sn system show very similar trends. The implications of these data are surprising. Either considerable densities of antistructure defects are possible or the $A15$ structures can accommodate vacancy or interstitial concentrations of 20 at.% and greater. This last possibility appears physically implausible. If we accept then that such a high density of antistructure defects is possible, we are faced with equally intriguing possibilities. For example, T_c's ~ 16 K are possible for Nb:Sn ~ 2.5. This ratio implies 5% of the sites on the Nb chains are occupied by Sn atoms. T_c therefore does not appear to be crucially dependent on the integrity of the Nb chains although some dependence clearly may exist.

An interesting correlation has emerged from the T_c versus stoichiometric dependences of Nb-Ge and Nb-Sn. T_c appears to be optimized at composition ratios as low as 2.7:1 instead of the canonical 3:1. It has been suggested[9] that oxygen impurities are needed to stabilize the high-T_c Nb_3Ge films and that oxygen can be incorporated in the $A15$ structure at high levels to compensate for the above stoichiometric variations. Our Rutherford-backscattering and nuclear-reaction studies show no evidence for this contention. The combined total of light impurities such as C, N, and O are at low levels (< 2 at.%) in the high-T_c films. It is, of course, well known that defects or impurities can stabilize phases. The present observation that T_c appears to be optimized at composition ratios of 2.7:1 instead of 3:1 may indicate that lattice stabilization is effected by the simple mechanism of replacing 3% of the Nb atoms with Ge or Sn atoms. Antistructure defects may be stabilizing the lattice. They do not, however, lead to large reductions in T_c.

In summary, therefore, the introduction of defects in the $A15$ superconductors produces a certain universality of behavior with regard to (a) T_c degradation, (b) formation of the saturated state, (c) lattice parameter expansion, and (d) resistance ratio correlations.[2,4,11] It seems unlikely that antistructure (antisite) defects alone are responsible for such universality. Probably any type of defect, in sufficient density, will affect T_c, for example. The lack of strong correlation of T_c with stoichiometry in Nb-Ge and Nb-Sn suggests that T_c is not crucially dependent on the integrity of the Nb chains. The integrity of the overall lattice structure must, however, be maintained; otherwise T_c will degrade as has been demonstrated in the present correlations.

Further descriptions of this work will be given elsewhere.[10] We are indebted to D. E. Cox and A. R. Sweedler for illuminating discussions, to A. R. Storm for the x-ray measurements, and to W. M. Augustyniak for expert technical assistance on the accelerator.

*Work at Stanford University supported under U. S. Air Force Grant No. AFOSR73-2435.

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