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Effects of composition and neutron irradiation on the superconducting properties of Nb_3Al

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Phase-equilibrium and neutron-irradiation studies have been carried out on the Nb-Al system in the *A*15 phase region. The *A*15 phase boundary extends from 20–24 at.% Al at 1730 °C, with a maximum T_c midpoint at 18.6 K. Irradiation with reactor neutrons produces large reductions in T_c, which are accompanied by decreases in the long-range order parameter S and increases in the lattice parameter a_0. These changes are completely reversible on annealing.

I. INTRODUCTION

The *A*15 phase of Nb_3Al was first reported by Wood *et al.*[1] and later found to be superconducting by Corenzwit.[2] As the transition temperature T_c and upper critical field at 4.2 K, H_{c2}, are both relatively high, 18.8 K[3] and 195 kOe,[4] respectively, considerable attention has been focused on the factors influencing superconductivity in this system.[5–8] Although the *A*15 phase has been known for some time, conflicting data exist as to its homogeneity range in the Nb-Al system and the mechanism of formation from the liquid. Lundin and Yamamoto[9] reported that the composition range of the *A*15 phase extended from 17 at.% Al at 1000 °C to 32 at.% Al at 1870 °C, the stoichiometric composition formed by a peritectic reaction of Nb solid solution and liquid at 1960 °C. Sveshnikov *et al.*,[10] however, concluded that the composition range was considerably narrower, extending from 19 at.% Al at 1000 °C to 26 at.% Al at 1730 °C. Moreover, the data indicated a peritectoid formation of the *A*15 phase from Nb solid solution and Nb_2Al at 1730 °C. Müller[5] placed the Al-rich phase boundary at 24.2 at.% Al at 1840 °C, in much better agreement with Sveshnikov *et al.* Recent work by Webb[11] also supports the narrower homogeneity range.

The dependence of T_c on composition has also been investigated by several workers.[5,8,12–14] The general trend observed is a decrease of T_c with increasing Nb concentration within the *A*15 phase region, although the details differ from worker to worker. The effect of long-range order on T_c has also received some attention.[6,13]

In this work we report the results of a study directed towards a better understanding of the superconducting properties of Nb_3Al and resolution of some of the conflicting data noted above. We present results on the homogeneity range of the *A*15 phase, the effects of composition and order on T_c, and the influence of irradiation with reactor neutrons on both the superconducting and structural properties. Unless otherwise stated, the formula Nb_3Al is taken to represent the *A*15 phase in the binary Nb-Al system. Stoichiometric Nb_3Al implies a ratio of 3Nb:1Al.

II. EXPERIMENTAL PROCEDURES

The samples were prepared by melting appropriate amounts of Nb powder and Al powder in a standard argon arc furnace. The powders were thoroughly mixed and pressed into pellets, with excess Al added to make up for weight losses during melting. After melting, the samples were submitted to a series of heat treatments with the objective of obtaining homogeneous, single phase, ordered specimens. In order to achieve this three different heat treatments were employed: (i) a high-temperature anneal (1400–2000 °C) for a relatively short time (5 min–12 h) to remove all traces of coring or segregation present in the as-cast specimens; (ii) a longer-term anneal (2h–8 days) in the temperature range (1000–1900 °C), to homogenize the samples. The second anneal proved to be important in obtaining reproducible results; (iii) a low-temperature anneal (750 °C) for periods of 2–70 days to enhance the degree of order. In addition, selected specimens were rapidly quenched (cooling rate about 10^3–10^4 °C/sec) from high temperatures into liquid gallium in a furnace previously described.[15] These samples were referred to as "quenched samples."

The samples were characterized by standard metallographic techniques and x-ray diffractometry. The compositions were derived from the nominal compositions assuming that all weight losses resulting from the various casting and heat treatments were due to loss of Al, and are believed to be correct to within ±0.5 at.%. In selected cases the composition was confirmed by electron microprobe analysis. Lattice parameters a_0 are accurate to $\pm 0.001-0.002$ Å. The degree of long-range order was determined in the manner previously described.[16]

Irradiation with reactor neutrons at 150 °C was carried out at the Brookhaven High Flux Beam Reactor (HFBR) as previously described,[17] and the fluence was determined using a flux of 1.0×10^{14} $n/\text{cm}^2\,\text{sec}$ ($E > 1$ MeV). Superconductivity was measured inductively using a low-frequency (17 Hz) technique, and T_c was determined with a calibrated Ge thermometer to ±0.1 K.

Specimens in the 19 to 27 at.% Al range quenched from temperatures between 1730 and 1960 °C did not yield single-phase *A*15 material as would be expected from the phase diagram of Lundin and Yamamoto.[9] Between 1830 and 1960 °C quenched samples of composition 24 at.% Al resulted in α-Nb solid solution, while samples quenched between 1750 and 1830 °C yielded $\alpha\text{-Nb}+\sigma\text{-}(\text{Nb}_2\text{Al})$ phases. Single-phase *A*15 samples could only be obtained by annealing below 1730 °C. These results are consistent with the phase diagram presented by Sveshnikov *et al.*[10] and the more recent work by Müller[5] and Webb[11] noted above.

Table I summarizes the heat treatments, transition temperatures, lattice parameters, and phases present for samples in the range 18.7 to 29.4 at.% Al. It is seen that, in order to obtain single-phase *A*15 specimens, high-temperature homogenization of the as-cast samples is essential.

Single-phase samples were obtained in the composition range 20.2 to 23 at.% Al. At 24.5 at.% Al, a small amount of σ phase (estimated to be 6 wt.% from the diffraction pattern) was detected, yielding a corrected composition of 24.1 at.% Al for the *A*15 phase. Beyond 25 at.% Al, the amount of σ phase rapidly increases, while the lattice parameter stays constant.

The T_c and a_0 data are plotted in Fig. 1 as a function of composition. From the behavior of a_0, we conclude that the Al-rich phase region extends from 20 to 24 (±0.5) at.% Al at 1730 °C. In this single-

TABLE I. Summary of heat treatment, T_c, and a_0 data for the Nb-Al system. N.M. = not measured; T_{ci} = onset; T_{cm} = midpoint.

Composition	Heat treatment	T_{ci} (K)	T_{cm} (K)	ΔT_c (K)	a_0 (Å)	Remarks
$\text{Nb}_{81.3}\text{Al}_{18.7}$	As cast	16.7	15.4	1.8	N.M.	$A15+\text{Nb}_{SS}$
$\text{Nb}_{81.3}\text{Al}_{18.7}$	10 min 1730 °C + 24 h 1240 °C + 48 h 725 °C	11.9	10.2	1.1	5.196	$A15+\text{Nb}_{SS}$
$\text{Nb}_{79.8}\text{Al}_{20.2}$	As cast	16.8	13.9	1.3	N.M.	$A15+\text{Nb}_{SS}$
$\text{Nb}_{79.8}\text{Al}_{20.2}$	42 h 1350 °C + 1 week 750 °C	15.8	10.5	3.6	5.196	*A*15
$\text{Nb}_{78.1}\text{Al}_{21.9}$	As cast	17.3	16.4	1.3	N.M.	*A*15
$\text{Nb}_{78.1}\text{Al}_{21.9}$	17 h 1550 °C + 1 week 750 °C	17.5	14.9	3.6	5.191	*A*15
$\text{Nb}_{77}\text{Al}_{23}$	As cast	17.2	17.1	0.1	N.M.	$A15+\sigma$
$\text{Nb}_{77}\text{Al}_{23}$	12 h 1650 °C + 203 h 750 °C	18.7	17.7	1.4	5.186	*A*15
$\text{Nb}_{75.5}\text{Al}_{24.5}$	As cast	17.5	17.3	0.1	N.M.	$A15+\sigma$
$\text{Nb}_{75.5}\text{Al}_{24.5}$	10 h 1700 °C + 1 week 750 °C	18.7	18.6	0.1	5.184	$A15+\sigma$
$\text{Nb}_{74.7}\text{Al}_{25.3}$	As cast	17.5	17.2	0.2	N.M.	$A15+\sigma$
$\text{Nb}_{74.7}\text{Al}_{25.3}$	10 h 1730 °C + 1 week 750 °C	18.8	18.6	0.2	5.183	$A15+\sigma$
$\text{Nb}_{73}\text{Al}_{27}$	As cast	17.5	17.0	0.6	N.M.	$A15+\sigma$
$\text{Nb}_{73}\text{Al}_{27}$	10 h 1730 °C + 1 week 750 °C	18.7	18.5	0.3	5.184	$A15+\sigma$
$\text{Nb}_{70.6}\text{Al}_{29.4}$	As cast	17.2	14.7	2.2	N.M.	$A15+\sigma$
$\text{Nb}_{70.6}\text{Al}_{29.4}$	10 h 1730 °C + 1 week 750 °C	18.7	18.4	0.3	5.184	$A15+\sigma$

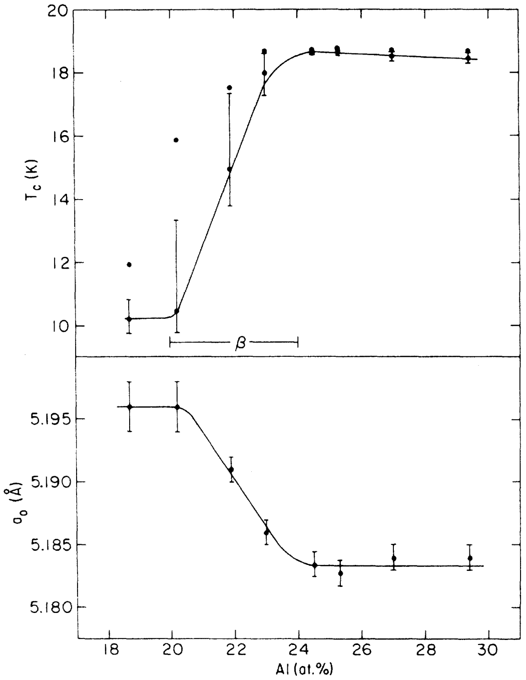

FIG. 1. T_c and a_0 vs composition for the Nb-Al system. Upper data points are T_c onsets, lower points are T_c midpoints, and error bars are transition widths. The homogeneity range of the $A15$ phase is indicated.

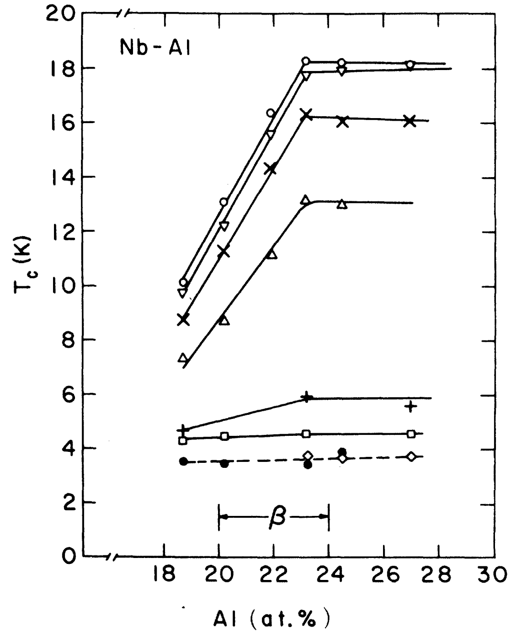

FIG. 2. T_c (midpoints) vs composition for Nb-Al alloys irradiated with reactor neutrons. Fluence levels (neutrons/cm^2, $E > 1$ MeV) as follows: unirradiated (○), 5×10^{17}(▽), 2.5×10^{18}(×), 5.8×10^{18}(△), 1.7×10^{19}(+), 2.5×10^{19}(□), 4.7×10^{19}(◇), 1.0×10^{20}(●). Homogeneity range of $A15$ phase (β) as indicated. Samples containing more than 24 at.% Al contain some σ phase.

phase region there is a strong compositional dependence of T_c midpoints amounting to about 2.7 K at.% Al, similar to other high-T_c Nb-base $A15$ materials.[18]

$A15$ compounds A_3B are characterized by long-range order parameters S_A and S_B for the two types of site. For the annealed sample containing 23 at.% Al, S_A and S_B were 1.00 ± 0.02 and 0.89 ± 0.02, respectively,[16] and thus correspond to as high a degree of order as possible for this composition, with all the Nb sites and 8% of the Al sites being occupied by Nb.

The effects of neutron irradiation as a function of composition are shown in Fig. 2 for fluences up to 1.0×10^{20} n/cm^2 ($E > 1$ MeV). All samples with different compositions were irradiated at the same time to ensure an equivalent dose. T_c is seen to decrease with increasing fluence for all compositions, but the rate of decrease increases with increasing Al concentration within the $A15$-phase region. Thus the T_c of a sample with 23.2 at.% Al decreased 5.5 K for a fluence of 5.8×10^{18} n/cm^2 while the T_c of another sample with 18.7 at.% Al decreased only 3.0 K for the same fluence. At high fluences, 1.0×10^{20} n/cm^2, T_c saturates at ~3.5 K and is essentially independent of composition.

The lattice parameter a_0, is shown in Fig. 3 as a function of composition for samples irradiated to 4.7×10^{19} n/cm^2, which is within the saturation region for T_c. For all compositions, an increase in a_0 is observed with increasing fluence. This increase is almost independent of composition, in marked contrast to the T_c depressions, which are composition dependent. The x-ray patterns for the neutron-irradiated specimens revealed several interesting features. In

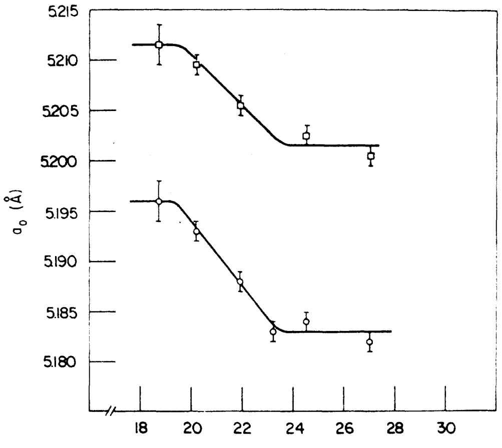

FIG. 3. a_0 vs composition for Nb-Al alloys unirradiated (□), and irradiated to a fluence of 4.7×10^{19} neutrons/cm^2, $E > 1$ MeV (○). Samples are not the same as those in Fig. 1.

common with most *A* 15 materials, no line broadening of any of the diffraction lines was observed to the highest fluence measured (4.7×10^{19} n/cm^2). Also, the intensity of those diffraction lines which are most sensitive to changes in the degree of long-range order showed a systematic decrease with increasing fluence, while the intensity of the other peaks changed relatively little. This observation indicates a decrease in the degree of long-range order with increasing fluence, which correlates with the decrease in T_c. Quantitative measurements of the degree of order for neutron-irradiated Nb_3Al have previously been reported.[17]

As observed for other neutron-irradiated Nb-base *A* 15 compounds, T_c and a_0 can be restored to their unirradiated values by appropriate annealing.[19] Figure 4 shows an isochronal annealing curve for several different Al compositions within the *A* 15-phase region. Recovery of T_c begins at about 450 °C for all compositions and is complete at 800 °C. In fact, T_c is even seen to be enhanced by about 1 K with respect to the unirradiated values in the 20.2 and 18.7 at. % Al samples. This was confirmed with an unirradiated control sample of the latter which was given the same annealing treatment but showed no enhancement of T_c. The slight decrease in T_c above 800 °C is probably associated with the precipitation of a second phase.

One final comment concerns the previous neutron-diffraction study of Nb_3Al,[17] in which the actual composition was taken as 26 at. % Al. This sample was arc melted, but was not given any high-temperature homogenization annealing treatment. Although in this way it might be possible to freeze in enough disorder to extend the *A* 15 phase boundary somewhat beyond 24–24.5 at. % Al, a figure of 26 at. % seems rather unlikely. We have accordingly reanalyzed the 1.25-Å neutron-diffraction data of Ref. 17 for an Al content of 25 at. %, with one difference in the model. Individual isotropic temperature factors were assigned to the Nb and Al sites in the irradiated samples and allowed to vary instead of being held at the unirradiated values. The results of least-squares refinements are summarized in Table II, together with the T_c's and a_0's. The main effect of the 1% change in composition is a correlated decrease of about 0.03 in the occupation parameter *x*, which corresponds to an increase in S_A of about 0.04, and a decrease in S_B of about 0.01. This still represents an appreciable amount of residual disorder introduced in the arc-melting process. Attempts to anneal out this disorder most likely lead to precipitation of σ phase

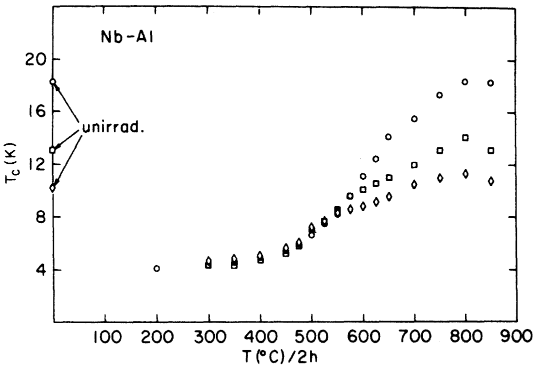

FIG. 4. T_c dependence on temperature for isochronal annealing of Nb-Al alloys. Irradiated to a fluence of 4.7×10^{19} neutrons/cm^2, $E > 1$ MeV. Compositions (at. % Al) as follows: 23.2 (○), 20.2 (□), 18.7 (◇). T_c's of unirradiated samples are indicated on the ordinate.

TABLE II. Reanalysis of 1.25-Å neutron-diffraction data for Nb_3Al in Ref. 17 with an assumed composition of 25 instead of 26 at. % Al. *x* is defined in the formula $(Nb_{3-x}Al_x)[Al_{1-x}Nb_x]$. *R* and R_w are crystallographic *R* factors. $R = \sum w|I_{\text{obs}} - I_{\text{calc}}| / \sum wI_{\text{obs}}$; $R_w = [\sum w(I_{\text{obs}} - I_{\text{calc}})^2 / \sum wI_{\text{obs}}^2]^{1/2}$; $w = 1/\sigma^2(I_{\text{obs}})$. NO is the number of observations. $\langle u^2 \rangle$ is related to the temperature factor *B* through the expression $\langle u^2 \rangle = B/8\pi^2$.

	Neutron fluence (n/cm^2)		
	0.0	5.8×10^{18}	1.2×10^{19}
T_c (K)	18.6	13.6	9.6
a_0 (Å)	5.183	5.191	5.195
x	0.064(13)	0.137(23)	0.195(17)
$\langle u^2 \rangle_{\text{Nb}}$ (Å^2)	0.0073(8)	0.0060(14)	0.0061(9)
$\langle u^2 \rangle_{\text{Al}}$ (Å^2)	0.007(2)	0.005(4)	0.006(3)
R	0.020	0.043	0.024
R_w	0.030	0.059	0.038
NO	19	14	13
$S_A (=S_B)$	0.91_5	0.81_7	0.74_0

and a decrease in the Al content of the $A15$ phase.

Another point to note in Table II is that the mean-square displacements $\langle u^2 \rangle$ do not change as a function of fluence within the estimated errors, which are about 0.001 Å^2 for the Nb site. The behavior of neutron-irradiated Nb_3Al and V_3Si (Ref. 20) is therefore different from that of thin films of α-irradiated V_3Si (Ref. 21) in this respect.

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