

Superconductivity and atomic ordering in neutron-irradiated Nb₃Al[†]

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We have utilized the technique of neutron-induced disorder to study the effect of atomic ordering on the superconducting transition temperature T_c of the *A*-15 compound Nb₃Al. Large depressions in T_c are observed when Nb₃Al is irradiated with high-energy neutrons ($E > 1$ MeV) at 140 °C. For samples whose value of T_c before irradiation was 18.7 K no superconductivity was observed to 1.4 K after irradiation to a fluence of 1.4×10^{19} n/cm². The widths of the transition temperatures remain constant as T_c is depressed and T_c is recovered by annealing at 750 °C after irradiation. The Bragg-Williams long-range-order parameter S was determined by least-squares analysis of neutron-diffraction data from powdered samples both before and after irradiation. A reduction in S of 18% is observed for samples irradiated to a fluence of 1.2×10^{19} n/cm². For the same fluence T_c is depressed to 52% of its value before irradiation. The lattice parameter a_0 of the *A*-15 phase expands upon irradiation, increasing from 5.183 Å for unirradiated samples to 5.200 Å for samples irradiated to 5.0×10^{19} n/cm². The results are discussed in terms of *A*-site occupation in the *A*₃*B* *A*-15 structure and extrapolations of T_c for complete order are considered.

I. INTRODUCTION

The effect of atomic ordering on the superconducting properties of compounds having the *A*-15 (β -W) structure has received considerable experimental and theoretical attention in recent years.¹⁻⁶ The view that has emerged from these studies is that within a given system, the highest transition temperature is obtained for a compound that exhibits the maximum degree of order, i. e., *A* sites occupied only by *A* atoms and *B* sites occupied only by *B* atoms in the *A*₃*B* phase.⁷ This is generally found to be the case when the *A* atom is V or Nb and the *B* atom is selected from either group IIIA or IVA of the Periodic Table. Coupled with the concept of maximum order is the notion of *A*-chain integrity arising from the fact that the *A*-15 structure exhibits chains of *A* atoms arranged in a three-dimensional orthogonal array such that the distance between atoms along the chain is smaller than the distance between atoms in different chains.⁸ For a given system, the maximum T_c is obtained by occupation of the *A* sites along the chain by *A* atoms. Introduction of *B* atoms into the chains breaks the continuity of the chain and results in a lowering of T_c . The underlying mechanism for this depression of T_c is presumed to be the sensitivity of the density of states at the Fermi level to the continuity of the *A* chains.^{5,9,10} Some recent low-temperature heat-capacity measurements on low- T_c ($T_c < 12$ K) Nb- and V-base *A*-15 compounds lend support to this concept.^{3,4,11}

From an experimental point of view, the study of the effect on T_c of atomic ordering in *A*-15 compounds is faced with several difficulties. It is necessary to disorder the material homogeneously in such a way that the stoichiometry remains un-

changed and the width of the superconducting transition, ΔT_c , remains fairly narrow. Constancy of composition is important because T_c in many *A*-15 systems is dependent on stoichiometry,¹² so that any changes in T_c could not be ascribed unambiguously to disorder if the composition were to vary. Relatively narrow transition widths are required if a specific value of T_c is to be associated with a given degree of order.

The usual manner of producing disorder in *A*-15 materials is by quenching from an elevated temperature. In this procedure a sample is quenched from a suitable temperature, usually above 600 °C, to a much lower temperature as rapidly as possible in the hope of quenching or "freezing in" the disorder present at the higher temperature. The degree of disorder produced in this fashion depends on the particular system under consideration but with the exception of a few cases, such as V₃Au,⁴ is relatively small. For many systems of interest, e. g., Nb₃Al, Nb₃Sn, and Nb₃Ga, annealing temperatures higher than 1000 °C result in the precipitation of second phases which tends to lower T_c .^{12,13} Thus only in certain cases is quenching a satisfactory technique. Another procedure used is that of substitutional alloying, by which means disorder is introduced by progressively replacing one of the components in the *A*₃*B* phase by a third element rather than by interchanging the positions of the atoms. This approach can yield ambiguous results as it is often impossible to separate the effect of disorder from the chemical effect due to alloying.

In this work, we have utilized the technique of neutron-induced disorder to study the effect of disorder on the superconducting properties of *A*-15 compounds.^{14,15} Atomic rearrangement is brought about as the result of displacement collisions be-

tween energetic neutrons and the atoms of the sample. This technique has several advantages over the other procedures discussed above. First, the disorder produced in this manner is homogeneous because the cross sections are small and all parts of the sample are exposed to a uniform neutron flux. Relatively narrow transition widths are thus obtained. Second, apart from the creation of negligibly small amounts of new elements, the composition of the alloy remains unchanged as disorder is produced, eliminating any ambiguity in interpreting the results owing to compositional changes. Third, we have found that the T_c of the Nb-base high- T_c ($T_c > 18$ K) A-15 compounds is quite sensitive to high-energy-neutron irradiations.^{14,15} It is therefore possible to study the effects of disorder for a wide range of T_c values. There are also disadvantages to this technique. One is that the samples are radioactive after irradiation. The amount of radioactivity depends on the particular elements, the quantity used, and the time of irradiation, but usually is sufficiently large to require special handling techniques. Access to a reactor with relatively high flux, $\sim 10^{14}$ n/cm² sec, is also necessary if the irradiations are to be completed in a reasonable time. The irradiations also cause other effects besides displacement collisions, e.g., creation of vacancies, interstitials, and atoms of new elements.

We have chosen to investigate atomic ordering in the A-15 structure by making a neutron-powder-diffraction study on irradiated samples of Nb₃Al. Nb₃Al has a relatively high T_c (18.7 K) similar to the other high- T_c A-15 Nb-base compounds, Nb₃Sn,¹⁶ Nb₃Ga,¹³ Nb₃(AlGe),¹⁷ and Nb₃Ge.¹⁸ The difference in the thermal-neutron scattering of Nb and Al is large, so that changes in the intensities of peaks in the neutron-diffraction pattern are quite sensitive to the degree of disorder. The use of neutrons rather than x rays eliminates ambiguities about the scattering factors and the data are much less susceptible to preferred-orientation effects. Furthermore, it is possible to prepare almost-single-phase Nb₃Al, thereby greatly simplifying the interpretation of the diffraction data.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

The samples were prepared by arc melting pressed powder compacts of 99.95% Nb and 99.9% Al powders in a high-purity argon arc furnace using a nonconsumable tungsten electrode. The powders were pressed to about 50,000 psi and melted several times; excess Al was added to compensate for Al losses during melting. Two separate samples were prepared, designated as Nb₃Al(I) and Nb₃Al(II), weighing about 4 and 8 gms, respectively. After casting, the samples were wrapped in Ta foil,

sealed in quartz under $\frac{1}{2}$ atm of ultrahigh-purity (UHP) helium, and annealed for 50 h at 750 °C.

A portion of Nb₃Al(II) was analyzed to determine the amount of Al and Nb present. Aluminum was determined by atomic absorption spectroscopy while Nb was precipitated as an organic complex which was ignited to the oxide and weighed.¹⁹ The accuracy of the Al determination was 2% and relative precision of the Nb 0.3%. This information, together with the amount of second phase present, obtained from the neutron-diffraction data, allows the stoichiometry of the A-15 phase to be determined. Spectrographic analysis was also carried out to check the concentration of impurities in the sample.

Debye-Scherrer x-ray powder patterns were taken before and after irradiation with a 114.5-mm camera using Ni-filtered CuK α radiation. By using relatively short exposure times, about 1 h, and very small quantities of material ~ 1 mg, it was possible to decrease the fogging of the film due to the γ -radiation background from the irradiated samples to such a level that a clear diffraction pattern for all samples was obtained. The lattice parameter a_0 of the A-15 phase was determined by a $\cos^2\theta$ extrapolation utilizing reflections in the back-reflection region, to an accuracy of ± 0.001 Å.

B. Irradiations

To prepare the samples for irradiation portions of Nb₃Al(I), crushed to -100 mesh, were sealed in 4-mm quartz tubes about 1.9 cm long under $\frac{1}{2}$ atm of UHP helium exchange gas. In this manner it was possible to measure T_c and to carry out annealing studies after irradiation without removing the radioactive sample from the quartz tube. Keeping the samples in quartz tubes was also found very effective in minimizing radioactive contamination due to any unforeseen difficulties. Nb₃Al(II) was crushed before annealing to -100 mesh and pressed into a disk 0.635 cm in diameter and 2.22 cm long weighing about 3 g, as relatively large samples are required for the neutron-diffraction analysis. Several portions of Nb₃Al (II) were removed after annealing, sealed in quartz tubes as described above, and used for T_c determinations.

The irradiations were carried out in the Brookhaven High Flux Beam Reactor (HFBR). The quartz tubes were wrapped in Al foil, and placed in Al capsules designed to accommodate up to eight samples at a time. Aluminum foil was used to promote thermal contact between the quartz sample tubes and the Al capsules which were immersed in the reactor's cooling water. The measured temperature of the samples during irradiation was 140 °C. All irradiations were carried out under as nearly identical conditions as possible. The same thimble was used (V15) for all irradiations and the

fluence was determined by multiplying the time of an irradiation by the fast flux ($E > 1$ MeV), which is known to be $(1.0 \pm 0.5) \times 10^{14}$ n/cm² sec. As the irradiation thimble is located near the core of the reactor, the samples were exposed to the whole neutron spectrum of the reactor. However as it is unlikely that thermal neutrons cause sufficient damage to affect the superconducting properties, only the fast flux, $E > 1$ MeV, is considered here.

C. Determination of long-range order

The degree of long-range order (LRO) before and after irradiation was studied by neutron-diffraction analysis on powdered samples. All measurements were made on Nb₃Al(II).

The composition of the sample may be written as $(\text{Nb}_{3-x}\text{Al}_x)[\text{Al}_{1-x-y}\text{Nb}_{x+y}] = \text{Nb}_{3+y}\text{Al}_{1-y}$, where the round and square brackets denote Nb and Al sites, respectively. The parameter y determines the departure from the ideal stoichiometric ratio of 3Nb/1Al and may be positive or negative depending on whether the alloy is Al poor (< 25 at.%) or Al rich (> 25 at.%). The parameter x determines the fractional occupation of the Nb and Al sites by a particular atomic species. The parameters x and y can be related to the conventional Bragg-Williams long-range-order parameter S by noting that for nonstoichiometric compositions one must assign different values of S to each crystallographic site as pointed out by Van Reuth and Waterstrat.²⁰ In our case we may define an order parameter for the Nb or A sites, S_A , and for the Al or B sites, S_B , in the following manner:

$$S_A = \frac{P_A - \Gamma_A}{1 - \Gamma_A} = 1 - \frac{4x}{3(1-y)} \quad (1)$$

and

$$S_B = \frac{P_B - \Gamma_B}{1 - \Gamma_B} = 1 - \frac{4(x+y)}{3+y} \quad (2)$$

where $P_A = (3-x)/3$ is the fraction of A sites occupied by A atoms, $P_B = 1-x-y$ is the fraction of B sites occupied by B atoms, $\Gamma_A = (3+y)/4$ is the fraction of A atoms in alloy, and $\Gamma_B = (1-y)/4$ is the fraction of B atoms in alloy. We note that for stoichiometric alloys (i.e., $y=0$) $S_A = S_B$. The deviation from stoichiometry, y , was determined by chemical analysis, which together with the amount of impurity phase present fixes the stoichiometry of the A -15 phase.

In order to determine x , and hence either S_A or S_B , from a diffraction experiment it is necessary to take into account several structural parameters. The A -15 structure has the space group $Pm\bar{3}n(O_h^2)$ with the A atoms in the $6(c)$ sites at $\frac{1}{4}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{4}0$, $0\frac{1}{2}\frac{1}{4}$, $\frac{3}{4}0\frac{1}{2}$, $\frac{1}{2}\frac{3}{4}0$, $0\frac{1}{2}\frac{3}{4}$ and the B atoms in the $2(a)$ sites at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The latter have point symmetry $m\bar{3}$ and the corresponding Debye-Waller

temperature factor is isotropic, denoted by β . However, the Debye-Waller factor for the $6(c)$ sites, which have point symmetry $\bar{4}2m$, is anisotropic with two terms, β_{11} and β_{33} . The corresponding structure factor may therefore be written as

$$F = b_B(1 + e^{2\pi i(h/2+k/2+l/2)})e^{-\beta(h^2+k^2+l^2)} \\ + 2b_A[(e^{2\pi i(h/4+l/2)})e^{-[\beta_{11}(h^2+l^2)+\beta_{33}h^2]} \\ + (e^{2\pi i(k/4+h/2)})e^{-[\beta_{11}(h^2+l^2)+\beta_{33}k^2]} \\ + (e^{2\pi i(l/4+k/2)})e^{-[\beta_{11}(h^2+k^2)+\beta_{33}l^2]}], \quad (3)$$

where b_A and b_B are the average scattering amplitudes of atoms in the A and B sites, respectively, and h, k, l , have their usual crystallographic meaning. We can express b_A and b_B in terms of the scattering amplitudes of Nb and Al: $b_A = [(3-x)/3]b_{\text{Nb}} + (x/3)b_{\text{Al}}$ and $b_B = (1-x-y)b_{\text{Al}} + (x+y)b_{\text{Nb}}$. We have used values of $(0.711 \pm 0.004) \times 10^{-12}$ and $(0.345 \pm 0.001) \times 10^{-12}$ cm for b_{Nb} and b_{Al} , respectively, from a recent tabulation.²¹ For a stoichiometric alloy, i.e., $y=0$, in which the temperature factors are assumed to be zero, Eq. (3) yields the structure factors given by Van Reuth and Waterstrat in their Table 4.²⁰ Only a simple substitutional order-disorder model of the above type was considered, no attempt being made to allow for interstitial or vacancy types of disorder.

Neutron data were collected with neutrons of 2.46-Å wavelength from the (002) reflection of a pyrolytic graphite monochromator. Contributions from higher-order reflections were reduced to negligible proportions by means of a pyrolytic graphite filter.^{22,23} In addition data were collected with neutrons of 1.25-Å wavelength from the (311) reflection of a germanium monochromator in conjunction with a pyrolytic graphite analyzer in the (004) position for improved resolution at high angles. Half-wavelength contamination is absent in this case, and contributions from higher-order reflections were negligible.

In the angular region covered by the spectrometer the 2.46-Å data consisted of six reflections derived from Nb₃Al, together with a number of small impurity peaks which could all be indexed as arising from Nb₂Al. The strongest of these peaks was about 2% of the intensity of the strongest Nb₃Al peak. The peak-to-background ratios are quite favorable in this system and the sensitivity limit for detection of the Nb₂Al phase is about 0.05%.

The first problem in the data analysis was to correct for the impurity phase, and this was successfully accomplished by simultaneous least-squares refinement of the integrated intensity data from both phases by means of a computer program which allows overlapping peaks in a powder pattern to be included. The peaks were assigned standard errors of between 2 and 6% of the intensities depending on factors such as background and overlap, or in the

case of the weak peaks simply the statistical error when this was greater than 6%. Absorption corrections were negligible ($\mu R < 0.1$) and no preferred-orientation effects were noted. The structural parameters of Nb_2Al were fixed at the values reported by Brown and Forsyth.²⁴

For the 2.46-Å data, good intensity agreement was obtained with three variables: instrumental scaling constants for each phase (Nb_3Al and Nb_2Al) and the parameter χ . Agreement was not significantly improved by the introduction of temperature factors or deviations from perfect order in the Nb_2Al phase. From these results and application of the standard powder intensity formula,²⁵ the volume fraction of Nb_2Al was determined.

Refinement of the 1.25-Å data was next undertaken. In this case, there were 19 resolved peaks and in order to obtain good agreement between observed and calculated intensity values, it was necessary to include temperature factors. The variables in this case were thus χ , β , β_{11} , β_{33} , and the instrumental scale factor. The data collected at 1.25 Å were corrected for the presence of the Nb_2Al phase based on the results of the 2.46-Å refinement.

Data were collected in a similar fashion from the irradiated sample but since the radiation levels were quite high (several R/hr), about 2.5 cm of lead shielding was required in the vicinity of the sample. The irradiated sample was enclosed in an aluminum capsule which gave some overlapping peaks on the diffraction pattern, so that fewer peaks were available in the least-squares refinement than for the unirradiated sample. Allowing for possible compositional errors, and errors in the values of b_{Nb} and b_{Al} , the maximum uncertainty in the order parameter should not exceed ± 0.02 .

D. T_c Determination

Superconductivity was detected by a mutual-inductance technique operating at a frequency of 37

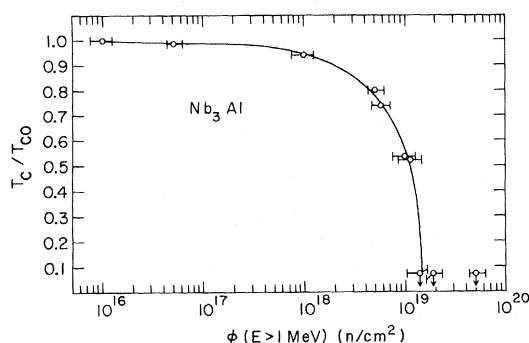


FIG. 1. Reduced transition temperature T_c/T_{c0} as a function of fluence ϕ ($E > 1$ MeV). The curve is drawn as a visual aid. Arrows indicate that no superconductivity was observed down to temperature indicated.

Hz. The sample was mounted on a single-crystal quartz holder and inserted into the secondary coil of a mutual-inductance pair which was located in the outer vacuum jacket of a double-vacuum-space Dewar. The double vacuum space enabled the measuring coils to be kept at 4.2 K while the sample could be warmed to temperatures above 4.2 K by a heater attached to the quartz. This avoided coil drift at high temperatures. The temperature above 4.2 K was determined by a 470- Ω Allen-Bradley carbon thermometer which was calibrated during each run against superconductors with known T_c 's. Below 4.2 K, the temperature was determined by monitoring the vapor pressure of liquid He⁴.²⁶ The accuracy of the T_c 's are ± 0.2 K.

III. RESULTS

A. Sample characterization

The results of the chemical analysis of $\text{Nb}_3\text{Al(II)}$, coupled with the determination of the volume fraction of Nb_2Al present, gave the composition of the A-15 phase as $\text{Nb}_{0.741 \pm 0.005} \text{Al}_{0.259 \pm 0.005}$. The volume fraction of Nb_2Al was determined to be 1.6%. Separate chemical analyses for Ta and O gave values of 0.18 wt. % in each case.¹⁹ Spectrographic analysis gave the following impurities present: Fe, 1000 ppm; Si, 100 ppm; Mg, 50 ppm; Ba, 100 ppm; Cu, 50 ppm; and V, 100 ppm. These impurity levels are too small to be of any significance in the structure determination. The relatively large amount of Fe was traced to the original Al powder used as starting material and is not believed to be important as the T_c 's were in good agreement with previously reported values for Nb_3Al .^{12,27} The lattice parameter was 5.183 ± 0.001 Å for both $\text{Nb}_3\text{Al(I)}$ and $\text{Nb}_3\text{Al(II)}$, also in good agreement with previously reported values.^{12,28}

B. Transition temperature

The results of the effect of high-energy-neutron irradiation on the T_c of Nb_3Al is shown in Fig. 1. T_c is the onset of superconductivity after irradiation, while T_{c0} is the value before. T_{c0} for $\text{Nb}_3\text{Al(I)}$ and $\text{Nb}_3\text{Al(II)}$ was 18.7 ± 0.2 and 18.6 ± 0.2 K, respectively. For $\text{Nb}_3\text{Al(I)}$ and $\text{Nb}_3\text{Al(II)}$ 50% of the transition was completed within 0.2 and 0.7 K, and 90% within 1.8 and 1.9 K, respectively. These widths remained unchanged, within experimental error, after irradiation.

The depression of T_c up to a fluence of 10^{18} n/cm^2 is quite small, about 6% relative to the unirradiated value, but subsequently T_c is rapidly depressed as a function of fluence. For a fluence of 1.2×10^{19} n/cm^2 a depression in T_c of 48% is observed while for fluences in excess of 1.4×10^{19} n/cm^2 , no superconductivity is observed at all down to 1.4 K, the lowest temperature available in this experiment.

It is possible to recover T_c by annealing the ir-

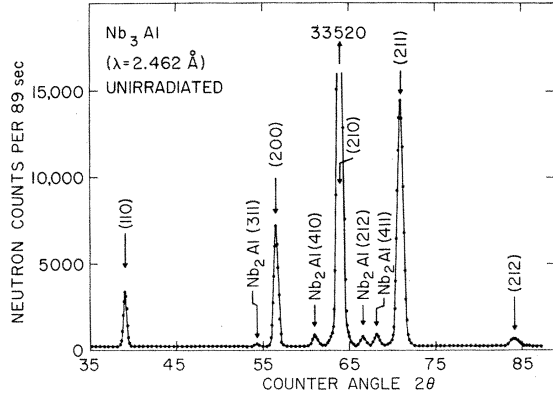


FIG. 2. Neutron-diffraction pattern for unirradiated $\text{Nb}_3\text{Al}(\text{II})$ obtained at $\lambda = 2.46 \text{ \AA}$ and room temperature.

radiated samples. After exposure to a fluence of $5.0 \times 10^{19} \text{ n/cm}^2$, a sample of $\text{NbAl}(\text{I})$, which was normal to 1.4 K, increased its T_c to 15.9 K after a 750 °C anneal for 10 min. Further annealing for 20 min, at the same temperature increased T_c to 16.2 K and an 80 min anneal resulted in a T_c of 17.7 K.

C. Long-range order

Figure 2 shows the diffraction pattern for unirradiated $\text{Nb}_3\text{Al}(\text{II})$ taken at 2.46 Å. The main peaks are due to the A-15 phase while the weaker peaks are due to the presence of the impurity phase, Nb_2Al . The strongest Nb_2Al peak was about 2% of

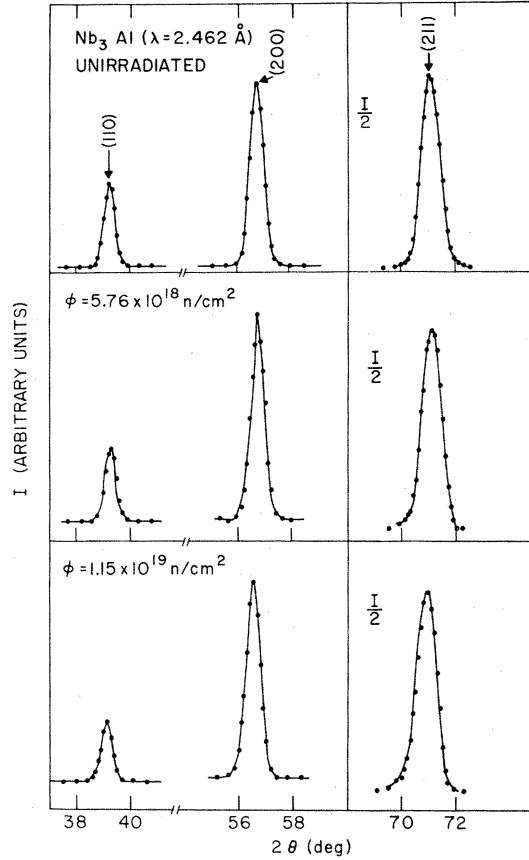


FIG. 3. Selected neutron-diffraction peaks for $\text{Nb}_3\text{Al}(\text{II})$ irradiated to different fluences.

TABLE I. Comparison of calculated and observed intensities for Nb_3Al at 1.25 Å. Observed intensities corrected for Nb_2Al .

(hkl)	$\phi = 0$			$\phi = 5.8 \times 10^{18} \text{ n/cm}^2$			$\phi = 1.2 \times 10^{19} \text{ n/cm}^2$		
	I_{calc}	I_{obs}	σ	I_{calc}	I_{obs}	σ	I_{calc}	I_{obs}	σ
110	452	450	15	214	213	11	94	91	6
200	1139	1114	40	725	725	35	388	398	15
210	6366	6380	150				overlap with Al		
211	3084	3063	100	1963	1906	80	1048	1015	50
220	117	122	10	56	51	6	25	36	6
310	172	178	10	81	94	8	36	39	4
222	1328	1311	40	758	705	30	379	369	9
320	2371	2365	50				overlap with Al		
321	2575	2533	100	1639	1575	70	875	877	50
400	1504	1515	50	922	933	30	481	450	22
411, 330	152	127	15				overlap with Al		
420	911	944	20				overlap with Al		
421	2975	2976	60	1772	1798	50	908	913	20
332	807	812	25	514	500	20	274	263	23
422	62	72	10	29	9	8	12	16	4
431, 501	204	211	15				overlap with Al		
432, 502	3171	3200	100	1888	2088	80	967	999	30
521	1183	1046	100	754	828	100	402	454	30
440	1514	1425	60	928	860	90			
R_w^2	0.027			0.059			0.044		

R_w^2 is defined as $[\sum w(I_{\text{obs}} - I_{\text{calc}})^2 / \sum w I_{\text{obs}}^2]^{1/2}$. $w = 1/\sigma^2$, where σ is the error assigned to the observed intensities.

TABLE II. Least-squares values of x in $(\text{Nb}_{3-x}\text{Al}_x)(\text{Al}_{1.04-x}\text{Nb}_{x-0.04})$ determined by least-squares refinement of neutron powder data collected at wavelengths of 2.46 and 1.25 Å.

	2.46 Å	1.25 Å	Average
Unirradiated	0.095 ± 0.011	0.097 ± 0.012	0.096 ± 0.012
$\phi = 5.8 \times 10^{18} \text{ n/cm}^2$	0.155 ± 0.012	0.180 ± 0.014	0.168 ± 0.013
$\phi = 1.2 \times 10^{19} \text{ n/cm}^2$	0.208 ± 0.012	0.230 ± 0.013	0.219 ± 0.013

the intensity of the strongest Nb_3Al peak.

Figure 3 shows selected peaks after successive irradiations. The intensity of the (110) peak, which is sensitive to the degree of ordering, is appreciably reduced with respect to the (200) and (211) peaks, which are relatively insensitive to ordering effects. It is immediately clear that the successive irradiations have produced increasing amounts of disorder. This is confirmed by the results of the least-squares refinements, shown in Tables I and II. Table I gives the results for the calculated intensities and compares them with the observed intensities. Table II gives the least-squares values of the parameter x from data collected at 1.25 and 2.46 Å.

In these refinements the temperature factors were held fixed at the values obtained for the unirradiated sample. Attempts to vary these for the irradiated samples did not result in any significant improvement, and also yielded rather high standard errors. The values of β , β_{11} , and β_{33} were 0.0053 ± 0.0012 , 0.0062 ± 0.0006 , and 0.0040 ± 0.0008 , respectively. These temperature factors correspond to rms amplitudes of vibration of 0.085 Å for the 2(a) sites and 0.092 and 0.076 Å for the 6(c) sites. It is interesting to note that the amplitude for the 6c(Nb) sites is significantly smaller in the direction of nearest neighbors in a given chain.

The Bragg-Williams order parameter S_A or S_B can be obtained from Eq. (1) or (2), respectively.

The value of the compositional parameter y is -0.04 , corresponding to 26 at. % Al, and the values for S_A and S_B are presented in Table III. Table III shows the percent of Nb sites occupied by Al atoms which in this case is just $100x/3$. The extrapolated values²⁹ of S given in Table III were obtained using the experimental result of Aronin³⁰ relating the order parameter to the fluence for Cu_3Au and Ni_3Mn . His result is $S = S_0 e^{-k\phi}$, where S_0 is the initial value of the order parameter before irradiation, S the value after exposure to a fluence ϕ , and k a proportionality constant. Using our experimentally determined values of S we obtain a value for k of $(1.8 \pm 0.5) \times 10^{-20} \text{ cm}^2/\text{n}$, which can be used to generate S values for fluences where S was not measured directly.

The variation of S_A with T_c/T_{c0} is shown in Fig. 4. Also shown is the fractional occupation of Nb sites by Al atoms. We see that in the range $0.52 \leq T_c/T_{c0} \leq 1$, T_c is a linear function of S_A . The value of $T_c/T_{c0} = 0.52$ corresponds to a fluence of $1.2 \times 10^{19} \text{ n/cm}^2$, and for fluences greater than $1.4 \times 10^{19} \text{ n/cm}^2$ no superconductivity was detected down to 1.4 K. The values of S_A for fluences above $1.2 \times 10^{19} \text{ n/cm}^2$ are extrapolated values obtained as described above.

D. Lattice parameter

The x-ray Debye-Scherrer powder patterns are shown in Fig. 5 as a function of fluence. We see that up to a fluence of $5.0 \times 10^{19} \text{ n/cm}^2$, the highest used in this experiment, Nb_3Al retains the A-15 crystal structure, but that successive irradiations produce an expansion of the lattice. This is most easily seen by noting the evolution of the (630) reflection. For unirradiated Nb_3Al the lattice parameter is too small for this reflection to be accessible. As a_0 increases, the corresponding d values increase and the reflection moves to lower diffraction angles. After irradiation to a fluence of $5.0 \times 10^{19} \text{ n/cm}^2$, the lattice has expanded a suf-

TABLE III. Summary of data for unirradiated and irradiated Nb_3Al .

Fluence $\phi \text{ (n/cm}^2\text{)}$	$T_c \text{ (K)}$	x	A-site	B-site	Lattice parameter $a_0 \text{ (Å)}$	% of Nb sites occupied by Al atom
			order parameter S_A	order parameter S_B		
0	18.6	0.096 ± 0.012	0.88 ± 0.02	0.92 ± 0.02	5.183 ± 0.001	3.2
1.0×10^{18}	17.6		0.86 ^a	0.91 ^a	5.185 ± 0.001	3.6 ^a
5.8×10^{18}	13.6	0.168 ± 0.013	0.79 ± 0.02	0.83 ± 0.02	5.191 ± 0.001	5.6
1.2×10^{19}	9.6	0.219 ± 0.013	0.72 ± 0.02	0.76 ± 0.02	5.195 ± 0.001	7.3
1.4×10^{19}	normal to 1.4		0.68 ^a	0.72 ^a	not measured	8.3 ^a
1.9×10^{19}	normal to 1.4		0.62 ^a	0.65 ^a	not measured	9.8 ^a
5.0×10^{19}	normal to 1.4		0.35 ^a	0.37 ^a	5.200 ± 0.001	16.8 ^a

^aExtrapolated values—see text.

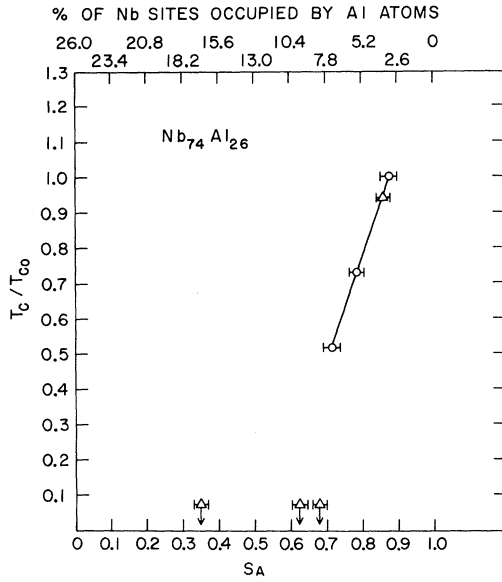


FIG. 4. Reduced transition temperature T_c/T_{c0} against A-site Bragg-Williams order parameter S_A for Nb_3Al . Also shown is percent of Nb sites occupied by Al atoms. Arrows indicate that no superconductivity was observed to temperature indicated. \circ , directly measured S_A ; Δ , extrapolated values (see text).

ficient amount so that the (630) reflection now lies within the accessible diffraction cone. The appearance of the (630) reflection, as well as the decrease in the Bragg angle of the (622) reflection, gives visual evidence of an expanding lattice, as is

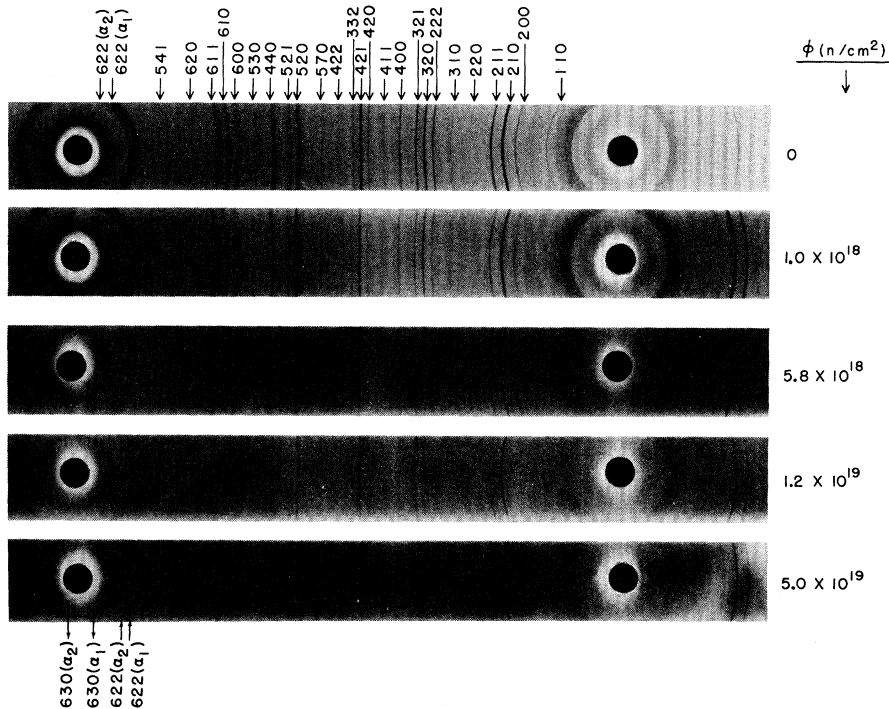


FIG. 5. Debye-Scherrer x-ray powder patterns for unirradiated and neutron-irradiated Nb_3Al .

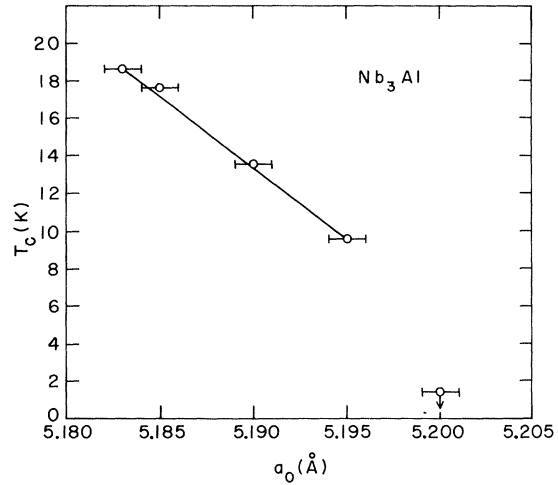


FIG. 6. Transition temperature T_c as a functional lattice parameter a_0 for neutron-irradiated Nb_3Al . Arrow indicates that no superconductivity was observed to temperature indicated.

confirmed by measurement of the film as shown in Table III. This expansion amounts to an increase in a_0 at a fluence of $5.0 \times 10^{19} \text{ n/cm}^2$ of 0.33% relative to its unirradiated value.

The variation of a_0 with T_c is shown in Fig. 6. We see an approximately linear dependence of T_c on a_0 down to a T_c value of 9.6 K, the latter corresponding to a fluence of $1.2 \times 10^{19} \text{ n/cm}^2$. For higher fluences no superconductivity was detected to 1.4 K.

IV. DISCUSSION

The results presented here (see Table III) show that the T_c of Nb_3Al is severely depressed when exposed to high-energy-neutron irradiation at 140°C . To the best of our knowledge the depressions of T_c are the largest ever observed in this material,³² amounting to more than 93% of the unirradiated value. These large depressions of T_c are also observed in other Nb-base high- T_c A-15 compounds when similarly irradiated with high-energy neutrons.^{14,15,31,33} We note that the transition width ΔT_c remains unchanged as T_c is depressed due to successive irradiations and also that T_c may be recovered by annealing at moderate temperatures (750°C).

On the basis of these results, it is reasonable to suppose that the principal effect of the high-energy-neutron irradiation is to bring about an exchange of atoms between the two kinds of sites in the lattice as a result of displacement collisions with the incident high-energy neutrons. This exchange results in a decrease in the degree of long-range order, which thereby causes a decrease in T_c .

The results of the neutron-diffraction studies presented here directly confirm this model and enable one to obtain a quantitative estimate of how sensitive T_c is to atomic ordering. We shall discuss our results in terms of the A-site order parameter S_A in order to emphasize the role that the A site plays in these materials. From an experiment of the type described here, it is not possible to determine whether the degree of order in A or B sites is more important with respect to T_c . However, other evidence exists which suggests that, at least to a first approximation, A-chain integrity is an important parameter affecting T_c .^{3,4,8,11}

If we regard the presence of Al atoms on Nb sites as an "impurity" on the A-site chain, then we can express the depression of T_c as a function of impurity along the chain. For Nb_3Al we obtain a depression rate, of 2.2 ± 0.2 K per % of Nb sites occupied by Al atoms, for $9.6 \leq T_c \leq 18.6$ K. In a previous study of neutron-irradiated Nb_3Sn , where S_A was not measured directly but inferred from a radiation-damage model, an initial depression rate of 3.3 K per % of Nb sites occupied by Sn atoms was obtained.¹⁴ These depression rates are quite large and indicate that the T_c 's of Nb_3Al and Nb_3Sn are very sensitive to atomic ordering. We can speculate that this holds true for the other Nb-base high- T_c A-15 compounds, Nb_3Ga and Nb_3Ge , as well. Similar depressions have also been observed in the low- T_c ($T_c = 3.22$ K) A-15 compound V_3Au when disordered by quenching.⁴ We also note that the magnitude of the depression rates observed here are usually associated with a pair-breaking or pair-weakening mechanism due to the presence

of magnetic impurities in superconductors.³⁴ However, in this case the underlying mechanism for the destruction of superconductivity is not known.

Exchange of atomic sites is not the only effect produced by neutron irradiation. We have also to consider the possibility of transmutations to other elements, the formation of vacancy-interstitial pairs, and the possibility of creating highly damaged or deformed regions, particularly at high fluences. The concentrations of any new elements formed due to thermal-neutron capture are calculated to be in the ppm range for the fluences used here,³⁵ and since T_c is recoverable upon annealing these impurities have no measurable effect on T_c . Although there have been no studies on vacancy-interstitial formation in materials such as Nb_3Al , results for the temperature of migration of interstitials in elements and compounds indicate that at the temperature of the irradiation, 140°C , there should be no free interstitials.³⁶ The concentration of the remaining vacancies is difficult to determine, but from studies on pure elements we estimate the < 1 at. % should remain for the fluences used here.³⁷

Previous work on neutron-irradiated Nb_3Sn at a fluence of 10^{18} n/cm^2 has revealed the presence of spots in electron micrographs³⁸⁻⁴⁰ about 100 \AA in diameter which have been interpreted as being highly deformed or amorphous regions.⁴⁰ However, both the x-ray- and neutron-diffraction patterns reveal that the Nb_3Al studied here is crystalline with a well-defined diffraction pattern of the A-15 phase, and no line broadening is observed even at the highest fluence used, 5×10^{19} n/cm^2 . We, therefore, conclude that if there are such regions in Nb_3Al , they occupy a comparatively small volume of the sample.

The spots that have been observed in Nb_3Sn have also been observed in Nb.⁴¹ However, the T_c of Nb is decreased only about 1% for a fluence of 2×10^{19} n/cm^2 .⁴² Furthermore, the superconducting properties of NbTi alloys are relatively insensitive up to fluences of 10^{20} n/cm^2 .^{43,44} Thus even if similar deformed or amorphous regions exist in Nb_3Al , it is likely that their effect on depressing T_c is much less important than the effect of interchange of atoms.

Irradiations to fluences of 1.4×10^{19} , 1.9×10^{19} , and 5.0×10^{19} n/cm^2 resulted in no observable superconductivity for $\text{Nb}_3\text{Al(I)}$ down to 1.4 K. This sharp drop in T_c above 1.2×10^{19} n/cm^2 was not observed for an earlier sample of Nb_3Al which showed a transition of 3.5 K for a fluence of 5.0×10^{19} n/cm^2 .¹⁴ This latter sample received no heat treatment after casting in contrast to the samples used in the present study and was mounted for irradiation in a different manner than the samples used here. There exists the possibility of some γ -ray heating

during irradiation due to the different mounting procedures which may have caused a slight increase in T_c . The possibility also exists that well annealed samples are more sensitive to irradiation than as cast samples. More irradiations are planned to investigate this possibility.

The observed lattice expansion of Nb_3Al can readily be understood on the basis of the atomic disorder produced by the irradiations. This expansion occurs because the radius of the Nb atom, 1.51 Å, is considerably larger than that of the Al atom, 1.39 Å,⁴⁵ in the *A*-15 phase so that the occupation of the Al sites by Nb atoms increases the "effective" radius of the Al site. This increase is not exactly compensated by the corresponding decrease in the effective radius of the Nb site, so that the lattice expands.

An approximate numerical estimate should be given by the hard-sphere model of the *A*-15 structure as discussed by Geller.⁴⁶ In this model the lattice parameter of the *A*-15 phase can be written as $a_0 = (r_A + r_B) 4/\sqrt{5}$, where r_A and r_B are the radii of the *A* and *B* elements in the *A*-15 phase. The above expression for a_0 assumes perfect order, and stoichiometry. However, when there is a certain degree of disorder one should calculate effective radii based upon the occupations of the particular site. In this case $r'_A = N_A r_A + N_B r_B$, where N_A is the fraction of *A* atoms on *A* sites and N_B is the fraction of *B* atoms on *A* sites and r'_A is the effective radius for the *A* site. An analogous expression holds for r'_B . Using the site occupations as determined from the present experiment we can calculate the increase in a_0 as a function of disorder. We find that for the disorder produced by a fluence of $1.2 \times 10^{19} \text{ n/cm}^2$, the calculated increase in a_0 is 0.3%, which may be compared to the measured increase 0.23%.

It should be noted that the magnitude of the observed lattice expansion is about the same as that caused by compositional variations in the *A*-15 phase of the Nb-Al system.^{12,28} Some caution is therefore necessary in using lattice parameters as a measure of composition in phase studies.

Finally, we would like to draw attention to the fact that there is a significant degree of disorder in the unirradiated sample (see Table III) although the measured values of T_c (18.6 K) and a_0 (5.183 Å) agree well with previously reported values.^{12,27} This implies that T_c for completely ordered Nb_3Al would be higher than the commonly accepted value of 18.7 K. In the present sample of $\text{Nb}_{0.74}\text{Al}_{0.26}$,

3.2% of the Nb sites are occupied by Al atoms, corresponding to a value of 0.88 for S_A . The maximum value of S_A for this composition is 0.95 and a linear extrapolation of the T_c -vs- S_A curve in Fig. 4 yields a T_c value of about 23 K for maximum order.

A small amount of disorder may help to stabilize the *A*-15 phase by increasing the effective radius of the Al in the *B* site to some minimum value. The instability of the Nb-base *A*-15 compounds containing *B* atoms smaller than Al (e.g., Ga, Ge, and Si) tends to support this idea. This would imply that the degree of disorder in Nb_3Ga and Nb_3Ge is greater than in Nb_3Al and therefore the T_c 's of fully ordered stoichiometric Nb_3Ga and Nb_3Ge would be considerably higher than the values of 20.3,¹³ and 23.2 K,¹⁸ respectively, which are the highest so far observed in these systems. It is clear that quantitative measurements of order parameters in Nb_3Ga and Nb_3Ge would be of great interest. Experiments of this type are presently under way.

V. SUMMARY

The superconducting properties of Nb_3Al are severely degraded when exposed to high-energy-neutron irradiation at 140 °C for fast fluences ($E > 1 \text{ MeV}$) above 10^{19} n/cm^2 . Similar behavior is also observed in other high- T_c Nb-base *A*-15 compounds. The transition widths remain constant as T_c is depressed, and T_c is recoverable by annealing at 750 °C.

The *A*-15 structure is retained as T_c is depressed. The Bragg-Williams order parameter S determined by least-squares refinement of neutron-powder-diffraction data decreases along with T_c . The rate of depression for Nb_3Al is $2.2 \pm 0.2 \text{ K per } \% \text{ of Nb sites occupied by Al atoms in the range } 9.6 \leq T_c \leq 18.6 \text{ K}$.

An expansion of the lattice parameter relative to its unirradiated value of 0.33% is observed for Nb_3Al irradiated to $5.0 \times 10^{19} \text{ n/cm}^2$. This expansion can be qualitatively understood in terms of the induced disorder and a hard-sphere model.

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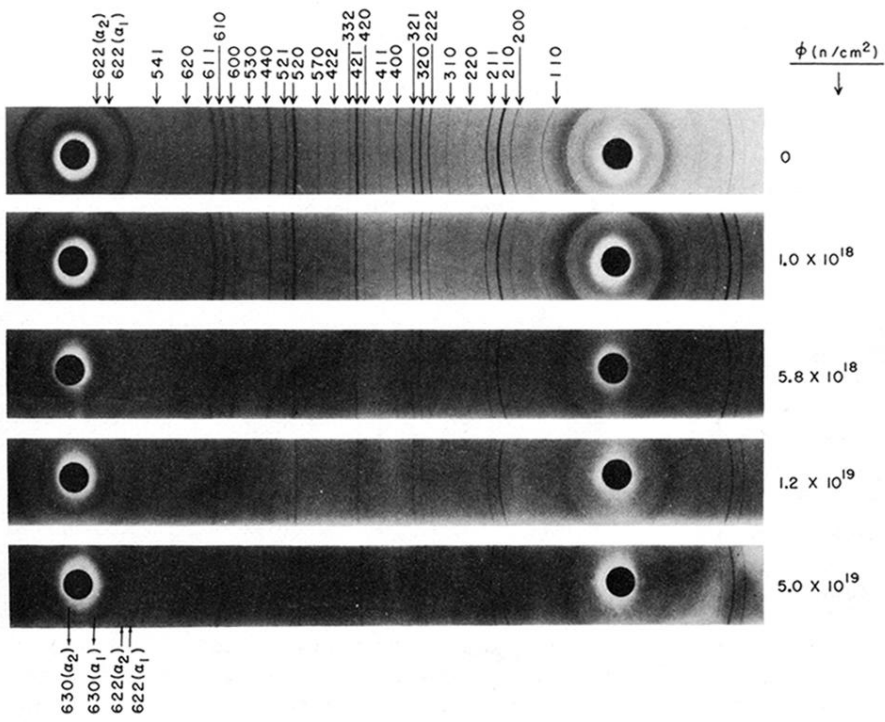


FIG. 5. Debye-Scherrer x-ray powder patterns for unirradiated and neutron-irradiated Nb₃Al.