Specific-heat studies of neutron-irradiated $A15$ Nb_3Al

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The specific heat of neutron-irradiated Nb_3Al has been measured in the temperature range 1.3–25 K for fluences of 1.3×10^{18} and 1.3×10^{19} n/cm^2 ($E > 1$ MeV). A reduction in the superconducting transition temperature is accompanied by an increase in transition width with increasing fluence. The Debye temperature increases 20%, and the electronic density of states shows a slight decrease that is within error limits, relative to the unirradiated material.

I. INTRODUCTION

There has been considerable interest in the effects of particle irradiation on the properties of $A15$ compounds in recent years. Previous studies[1–8] have revealed several trends including (1) a reduction in the superconducting transition temperature T_c, (2) a decreased electronic density of states, and (3) an increased lattice parameter, all relative to the unirradiated material. The unirradiated-state properties are restored upon annealing at temperatures where reordering by thermally generated vacancies occurs, and there is evidence to suggest that the effects of radiation damage on several properties are equivalent to those of the specimen's composition being off stoichiometry.[2–4]

We report specific-heat measurements on the $A15$ phase of Nb_3Al before and after irradiation with fast neutrons. These data are preceded by similar studies of Viswanathan and Caton[5] on V_3Si where interpretation of their results was complicated by possible uncertainties in the exact thermal histories of their irradiated samples. By comparison, the radiation-induced defects in Nb_3Al begin to recover at a significantly higher temperature[3] than in V_3Si and should therefore provide more reliable data. Also, it is a low-density-of-states $N(0)$ material while V_3Si has a high density of states. Thus, the behavior of $N(0)$ with fluence might be different in the two systems.

II. SAMPLE PREPARATION AND CHARACTERIZATION

The samples used in this study were prepared by arc-melting Nb and Al powders as described in detail in Ref. 2, followed by anneals of 10 h at 2030 K and 1 week at 1020 K. The resulting material had a composition of 24 $\pm$0.5 at.% Al, determined by electron microprobe analysis, and was at least 98% single phase, as indicated by x-ray diffractometry. The lattice parameter was 5.186 $\pm$0.001 Å which differs from values of 5.184 and 5.181 Å predicted for this composition by Moehlecke[2] and Kwo *et al.*,[9] respectively. Spitzli[10] reports 5.181 $\pm$0.005 Å for this composition.

Specific-heat data are reported for three samples with masses in the range 25–55 mg. Two were irradiated with fast neutrons in the Brookhaven High Flux Beam Reactor to total fluences of 1.3×10^{18} and 1.3×10^{19} n/cm^2 ($E > 1$ MeV), respectively. The third was not irradiated.

III. EXPERIMENTAL PROCEDURES AND RESULTS

Specific-heat measurements were made using the decay-constant method.[11] The apparatus is a small-sample calorimeter described fully in Refs. 12 and 13. Temperatures are determined by means of two calibrated Ge thermometers with an accuracy of $\pm$0.10 K. Corrections for self-heating from the radioactive samples did not exceed 0.5 K below 2 K and were insignificant above 4 K. The maximum addenda contribution to the total heat capacity was 40% at 1.3 K and 16% at 25 K. Similar measurements with high-purity Ge samples indicate an absolute accuracy for the present work of $\pm$4%. The internal precision of the data for the three samples is $\pm$2%.

The specific heat divided by the measured temperature, C/T, is plotted as a function of T^2 for each specimen in Figs. 1–3. Two features are immediately

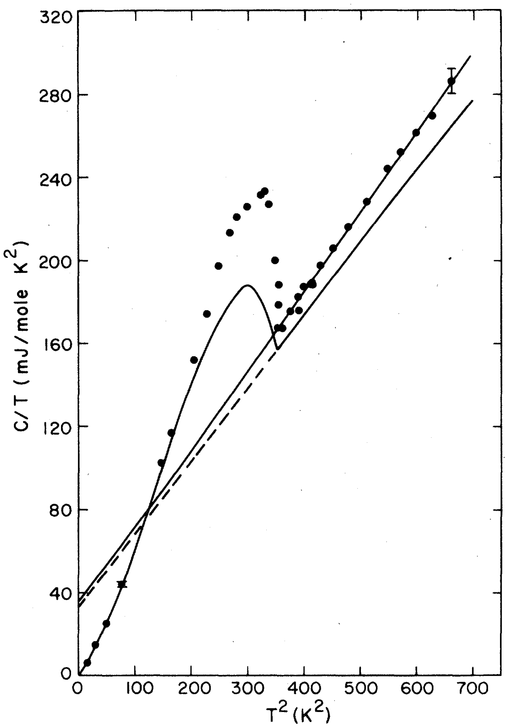

FIG. 1. Specific heat of unirradiated Nb_3Al. The lower curve is taken from Ref. 10 for comparison. The error bars on this figure and those following indicate the internal precision of $\pm 2\%$ of the data.

seen. For the irradiated samples, the superconducting transition temperature T_c is depressed, and the transition is broadened. Midpoint and onset T_c's and transition widths ΔT_c (equal to the onset T_c minus the peak T_c) are listed in Table I for each fluence. Inductively measured T_c's are shown for comparison

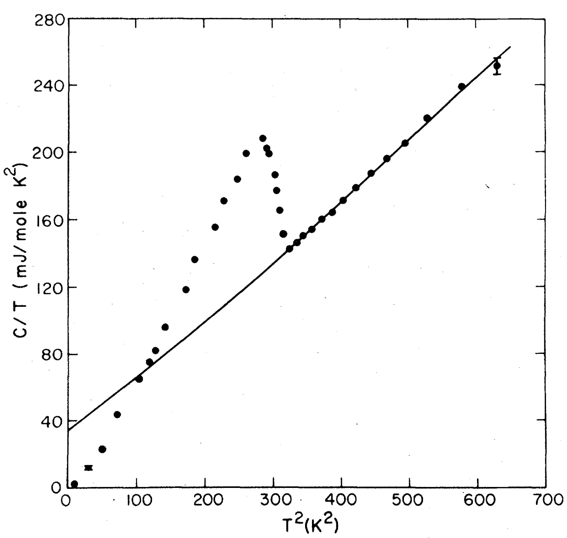

FIG. 2. Specific heat of Nb_3Al irradiated to a fluence of 1.3×10^{18} n/cm^2.

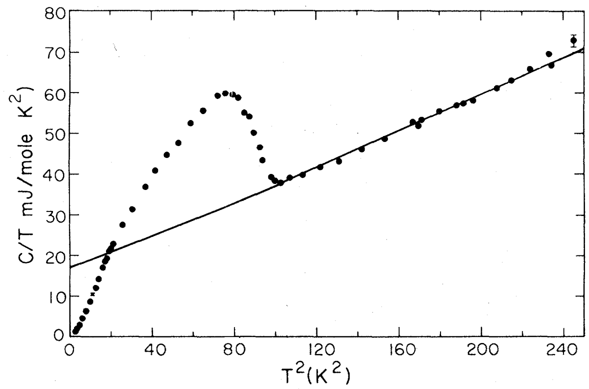

FIG. 3. Specific heat of Nb_3Al irradiated to a fluence of 1.3×10^{19} n/cm^2.

with the onset T_c's. A reduction in midpoint T_c of 6% occurs at the low fluence and of 50% at the higher dose. Substantial broadening is produced even at the low fluence, a phenomenon not seen[5] in irradiated V_3Si. This difference in behavior will be discussed below.

The specific heat of a normal metal at sufficiently low temperature may be approximated by

$$C/T = \gamma + \beta T^2 \quad , \tag{1}$$

where $C_e = \gamma T$ is the electronic contribution, and $C_L = \beta T^3$ is the lattice contribution. The normal-state specific heat of a high-T_c $A15$ compound often exhibits higher-order terms in this expansion, rendering a simple linear fit to C/T vs T^2 above T_c inadequate for determining γ and β. An alternative value of β can be found from the specific heat for $T << T_c$ since in this region, $C_e \cong 0$, and $C = C_L = \beta T^3$. In addition, for a second-order phase transition, the entropy S is continuous at T_c. Applied to a superconductor, this constraint, $S_n(T_c) = S_s(T_c)$, expressed in terms of the specific heat, is

$$S_n(T_c) = \int_0^{T_c} \frac{C_n}{T}\, dT = \int_0^{T_c} \frac{C_s}{T}\, dT = S_s(T_c) \tag{2}$$

and with a reasonable extrapolation of β from T_c to $T << T_c$, determines γ.

A. γ, $N(0)$, and Θ_D

For unirradiated Nb_3Al our value of γ derived from the entropy constraint is slightly larger than those of Spitzli[10] and Willens *et al.*[14] (See Table I.) This disagreement is probably due merely to our sample of Nb_3Al being slightly better ordered, as evidenced by the relative sizes and widths of the transitions in Fig. 1. Values of γ for our three samples appear in Table I and show a marked decrease for the

TABLE I. Parameters of Nb_3Al with varying radiation damage.

Fluence (n/cm^2)	Ref.	Midpoint T_c (K)	Onset T_c (K)	ΔT_c (K)	Inductive onset T_c (K)	γ ($mJ/mole\,K^2$)	Normal state Θ_D (K)	Low temperature θ_D (K)	λ	$N(0)$ (states/eV atom)	$H_c(0)$ (gauss)
0		18.7	18.8	0.6	18.7	36 ± 2	272 ± 5	283 ± 5	1.8 ± 0.2[a]	1.4 ± 0.2	4840 ± 50
0	10	18.3	18.7	1.4	· · ·	32 ± 0.6	280 ± 10	· · ·	· · ·	· · ·	· · ·
0	14	· · ·	18.8	0.5	· · ·	30 ± 3	290 ± 30	· · ·	· · ·	· · ·	· · ·
1.3×10^{18}		17.5	17.9	1.0	18.0	34 ± 3	276 ± 5	329 ± 5	1.8 ± 0.2[a]	1.3 ± 0.3	3972 ± 40
1.3×10^{19}		9.6	9.9	1.2	9.8	17 ± 3	325 ± 7	· · ·	0.7 ± 0.5	1.1 ± 0.2	1750 ± 20

[a]Reference 19.

higher fluence.

The electronic density of states at the Fermi surface, $N(0)$, in states/eV atom may be obtained from

$$\gamma = N(0)(1+\lambda)/0.1061 \tag{3}$$

and the Debye temperature Θ_D, from

$$\beta = 1944(4\times10^3)/\Theta_D^3 , \tag{4}$$

where γ is in $mJ/mole\,K^2$, β is in $mJ/mole\,K^4$, and λ is the electron-phonon coupling constant. Values for Θ_D determined from both the normal-state ($T > T_c$) and low-temperature data ($T << T_c$) are given in Table I. The low-temperature data are shown in Figs. 4 and 5 for zero and low fluence. For the higher fluence, the pure T^3 region was not attainable by pumping on the liquid ^4He. A comparison of normal-state Θ_D's for our samples indicates a pattern of lattice stiffening with damage.

For low-T_c superconductors, the electron-phonon coupling parameter λ can be calculated from the McMillan expression[15] with the Coulomb coupling constant $\mu^* = 0.10$. This equation is not valid for high-T_c superconductors, and for these cases λ must be determined from tunneling data. The estimates of λ in Table I for zero and low fluence are extrapolated for this composition from the tunneling results of Kwo and Geballe,[19] and the high-fluence value is found from McMillan's formula. The λ's are then used to calculate $N(0)$ via Eq. (3) with the results displayed in Table I. The variation of $N(0)$ with damage is within experimental uncertainty. It should be noted that Ghosh and Strongin[8] report $N(0) = 0.70$ states/eV atom from resistivity and critical-field data with $\lambda = 1.4$ and $\gamma = 30\pm2$ $mJ/mole\,K^2$. This value decreases to 0.5 states/eV atom for samples equivalent to ours irradiated to 1.3×10^{19} n/cm^2. This factor-of-2 difference is due to their estimates actually having units of states/eV atom spin.

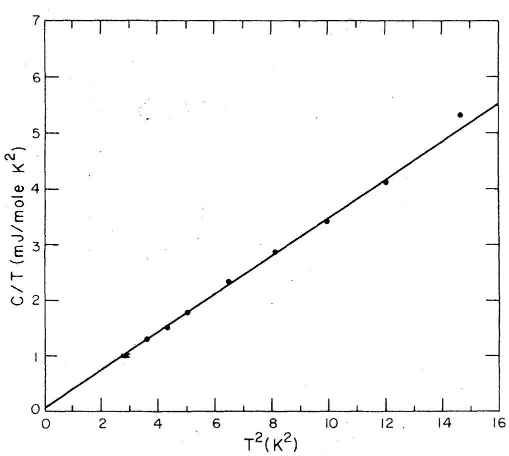

FIG. 4. Low-temperature specific heat of unirradiated Nb_3Al.

B. $H_c(0)$, $\Delta C/\gamma T_c$, and Δ

From the relation

$$\int_0^{T_c} (C_s - C_n)\,dT = \frac{VH_c^2(0)}{8\pi} , \tag{5}$$

the thermodynamic critical field $H_c(0)$ may be determined. The magnitude of the molar volume V is calculated from the lattice parameter of 5.186 Å for zero and low fluences. For the higher fluence, the lattice

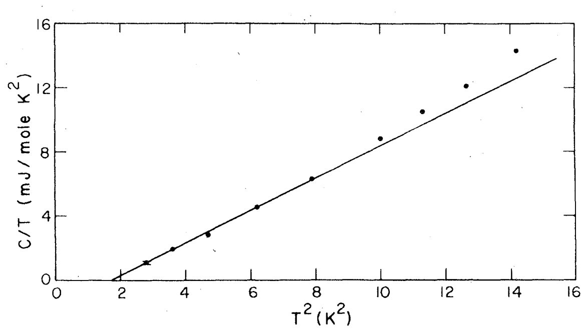

FIG. 5. Low-temperature specific heat of Nb_3Al irradiated to a fluence of 1.3×10^{18} n/cm^2.

parameter is estimated from the work of Moehlecke[2] to be 5.195 Å, based on fluence and composition. $H_c(0)$ decreases systematically with increasing fluence (Table I).

The size of the reduced specific-heat discontinuity $\Delta C/\gamma T_c$ is one measure of the electron-phonon coupling strength. For a broadened transition, there is some ambiguity in this parameter, and the values listed in column 2 of Table II are taken as the peak of the transition minus the normal-state extrapolation at the temperature of the peak, in each case.

A second parameter which specifies electron-phonon coupling strength is $2\Delta/k_BT_c$, the reduced energy gap. Since in the superconducting state, the BCS theory predicts for the electronic specific heat C_{es} the exponential form

$$C_{es}/\gamma T_c = a\exp[-\Delta(T)/k_BT] \ , \tag{6}$$

$\Delta(T)/k_BT_c$ should be the negative slope of $\ln C_{es}$ vs T_c/T. However, as pointed out in Refs. 16–18, electronic specific-heat data for superconductors typically do not obey Eq. (6) but yield the type of curves shown in Figs. 6–8 for our samples. It has been suggested[16,17] that $2\Delta(0)/k_BT_c$ may be found from the slope of $\ln C_{es}$ vs T_c/T near T_c, and this method works well[18] for many superconductors. For unirradiated Nb_3Al, this analysis yields $2\Delta/k_BT_c=5.6$, an unusually large value. However, tunneling results[19] extrapolated to this composition are also quite large, $2\Delta/k_BT_c \cong 5.0$. For irradiated Nb_3Al, the values listed in column 3 of Table II show a definite trend of decreased coupling as expected. Using these values to calculate $\Delta C/\gamma T_c$ for an ideally sharp transition via the relation

$$\Delta C/\gamma T_c = C_{es}/\gamma T_c - 1 \tag{7}$$

and Eq. (6), we obtain the magnitudes given in column 4, Table II, which are consistent with weakened electron-phonon coupling with increasing fluence. Another method of calculating $2\Delta/k_BT_c$ is by using the equation

$$\frac{2\Delta(0)}{k_BT_c} = \frac{H_c(0)}{T_c}\left[\frac{2\pi V}{3\gamma}\right]^{1/2} . \tag{8}$$

For these data Eq. (8) gives the results of column 5,

TABLE II. Electron-phonon coupling parameters.

Fluence (n/cm^2)	$\Delta C/\gamma T_c$ (Peak)	$2\Delta/k_BT_c$ (Slope)	$\Delta C/\gamma T_c$ (Sharp)	$2\Delta/k_BT_c$ [$H_c(0)$]
0	2.1	5.6	3.2	5.7
1.3×10^{18}	2.4	5.4	2.8	5.2
1.3×10^{19}	1.7	3.0	1.7	5.9

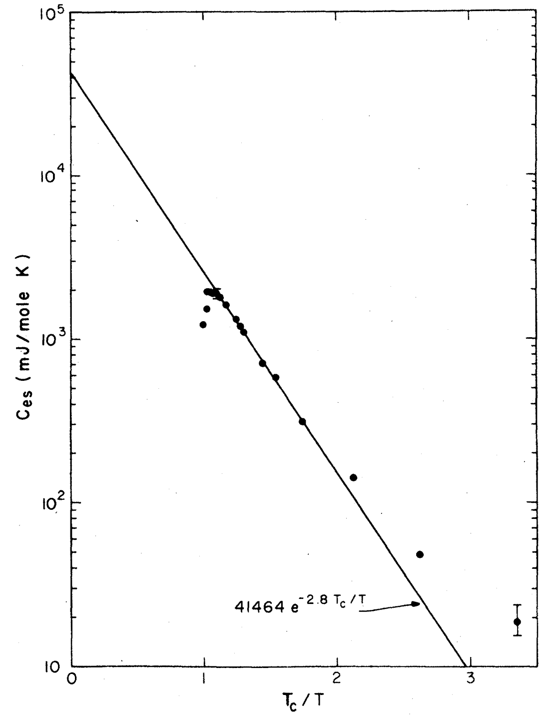

FIG. 6. Electronic specific heat of unirradiated Nb_3Al in the superconducting state.

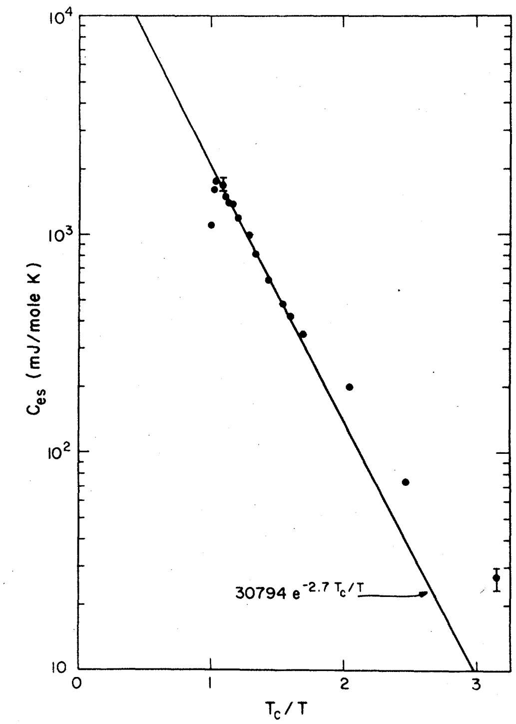

FIG. 7. Electronic specific heat in the superconducting state of Nb_3Al irradiated to fluence 1.3×10^{18} n/cm^2.

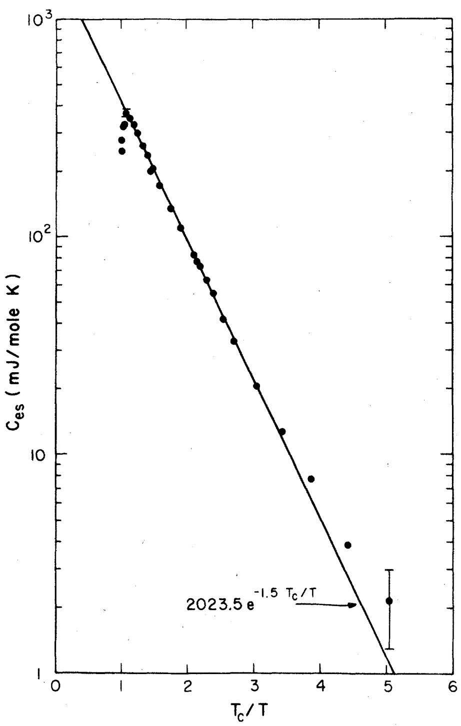

FIG. 8. Electronic specific heat in the superconducting state of Nb_3Al irradiated to fluence 1.3×10^{19} n/cm^2.

Table II. As in column 2, there is no clear pattern of decoupling, both columns indicating the persistence of strong coupling.

Data for a fourth Nb_3Al specimen subjected to a fluence of 2.6×10^{20} n/cm^2 were collected and analyzed. The transition temperature, expected to be ~4 K based on the fluence, was 7.1 K for both inductive and specific-heat transitions. In addition, the transition width was narrow, indicating that the sample was probably heated to the temperature of onset of recovery during irradiation. However, the Θ_D was 376 ± 5 K, following the trend of the other irradiated samples. Consistent with these results is the finding of Ref. 2 that the recovery in lattice parameter does not follow recovery in T_c, indicating that the lattice probably does not respond to annealing in the same manner as the electron gas. Further irradiation of this sample is planned to establish conclusively whether this behavior is attributable to annealing.

IV. DISCUSSION

The effects of neutron irradiation upon the superconducting and normal-state properties of Nb_3Al revealed by this specific-heat study may be summarized as follows: (1) The bulk transition temperature is depressed, and the transition width is broadened with irradiation. (2) The lattice is stiffened substantially by radiation damage. (3) A slight reduction in the density of states may occur in irradiated samples, but this trend is within experimental error.

The effect of neutron irradiation on the transition temperature of Nb_3Al and other *A* 15-type compounds has been the subject of several previous studies.[2–4,8] The reductions in T_c observed for the fluences used in this study agree well with those predicted in Refs. 2–4 based upon inductive measurements. Similar behavior was observed in a study[8] of resistively measured T_c in irradiated *A* 15's, including Nb_3Al, where the degree of damage was indicated by the residual resistivity. The specific-heat transition in neutron-irradiated V_3Si also exhibited T_c reduction and broadened with increasing fluence.[5] In samples with composition close to 24 at. % Al, Moehlecke[2] found no conclusive trend in inductive transition width in irradiated samples. However, an inductive measurement detects transitions in a small fraction of the material, whereas a specific-heat transition is attributable to the bulk.

Perhaps the most significant finding of this study is the enhanced Debye temperature with irradiation. This increase in Θ_D with damage in an *A* 15 compound has not been previously observed. The only other specific-heat work on a radiation-damaged *A* 15, that of Ref. 5 on V_3Si, showed no conclusive trend in Θ_D with damage. If radiation damage and varying stoichiometry are equivalent in their effects, then the lattice stiffening with increased departure from stoichiometry found by Junod *et al.*[20] in Nb_3Sn is analogous to our result. Ghosh and Strongin[8] also predict lattice stiffening with disorder in irradiated Nb_3Al based upon estimates of $\gamma/N(0)$ from resistivity and critical-field measurements.

The minimal effect of irradiation on the density of states is consistent with results for other low-density-of-states *A* 15 compounds, namely, Nb_3Ge and Mo_3Ge.[8] Conversely, high-density-of-states materials such as V_3Si (Refs. 5 and 8) and Nb_3Sn (Ref. 8) exhibit substantial reductions in $N(0)$ with damage. This pattern may be due to the position of the Fermi energy with respect to peaks in the electronic-density-of-states-versus-energy curve, which may become smeared with disorder. Additional support in favor of our results is a recent study[21] of $N(0)$ as a function of composition in Nb_3Al, which establishes no correlation.

It is tempting, in light of the data of columns 3 and 4 of Table II, to conclude in favor of reduced electron-phonon coupling in irradiated samples, as expected, but it is equally difficult to do so when there are conflicting results, as in columns 2 and 5. There is other evidence which suggests that decoupling does occur in irradiated Nb_3Al. The electron-phonon coupling constant λ, deduced from tunneling data,[19] decreases substantially with increased distance from stoichiometry. The normalized discontinuity $\Delta C/\gamma T_c$ in V_3Si decreased for high fluence but did not change appreciably for low fluence.[5] From resistivity and critical-field measurements, Ghosh and Strongin[8] predict reduced coupling in irradiated Nb_3Al. Further work is in progress to resolve this question.

V. CONCLUSIONS

The specific heat of Nb_3Al irradiated with fast neutrons has been measured. The superconducting transition temperature is depressed, and the transition width is broadened by radiation-induced disorder. Substantial lattice stiffening and only a slight reduction in the density of states are observed in the irradiated samples. No conclusive support for reduced electron-phonon coupling is apparent.

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