Superconductivity of proton-irradiated V_3Si

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(Received 13 October 1980)

Bulk samples of V_3Si were homogeneously irradiated by 35-MeV protons. Superconducting critical temperatures T_c, residual resistivities ρ_0, and upper critical fields H_{c2} were measured for magnetic fields up to 14 T and temperatures from 1.4 K up to T_c. The observed temperature dependence of H_{c2} is consistent with strong paramagnetic limiting and small spin-orbit scattering. Based on our collected data, estimates are provided for the electron-phonon coupling parameter λ and the band density of states $N(0)$. These estimates suggest that for radiation-damaged V_3Si a general relation of the form $\lambda = AN(0) - BN(0)^2$ exists, where A and B are positive constants.

I. INTRODUCTION

Materials possessing the $A15$ structure display the highest known critical temperatures T_c and critical current densities. In spite of very considerable research activity,[1,2] no clear theoretical understanding exists for the behavior of these superconductors. However, empirical regularities continue to emerge from work done on initially ordered $A15$ materials which are disordered by irradiation. Previous work has related T_c depression to disorder,[3–6] lattice constant,[6,7] and order parameter.[4,8,9] In addition, a number of papers have provided experimental estimates for electronic parameters, in particular, the band density of states $N(0)$.[10–16] In the case of V_3Si, such data are restricted to three reports,[10,14,15] two of which[10,15] are concerned mostly with lightly damaged samples. Reference 14 is similarly restricted to fairly lightly damaged samples ($T_c > 13$ K) and was performed on quench condensed films. It therefore appeared worthwhile to extend the work on irradiated V_3Si so as to encompass the complete available range of T_c depression ($2 \gtrsim T_c < 17$ K) on initially well-characterized bulk samples.

Radiation damage in our case was produced by 35 MeV protons at room temperature. A comparison of the defect structure to that of the more commonly used neutron irradiation[2] will be given.

In proton irradiation, the energies E of the primary knocked-on atoms (PKA) which are obtained by Rutherford scattering are distributed according to dE/E^2 from a minimum threshold energy of displacement up to a maximum E_m. In our case $E_m \approx 3$ MeV but the mean energy transferred to the PKA is only 0.3 keV. Thus, although some very energetic recoils are present, we may expect the damage to be mostly similar to that of electron irradiation. At low temperatures we expect isolated Frenkel pairs and small clusters. However, as we have ambient temperature irradiation, both interstitials and vacancies are mobile and we will have annihilation, replacement, and clustering of defects.

In neutron irradiation, the energies of the PKA which are produced by elastic collisions have a flat distribution. For reactor neutrons with an initial energy ≈ 1 MeV, $E_m \simeq 80$ keV and the mean energy transfer is $E_m/2 \simeq 40$ keV. This high energy of the PKA will produce at low irradiation temperature a defect cascade, i.e., a region of vacancies surrounded by an interstitial's rich cloud. At room temperatures, these defects will agglomerate probably into vacancy or interstitial loops.

Thus, most of the defects produced by proton or by neutron irradiation at low temperatures are different, but they change and become more similar at higher temperatures. However, the T_c depression in $A15$ superconductors, ΔT_c, at room temperature by either charged particle or neutron irradiation are equivalent.[2] Quantitatively, ΔT_c is directly given by the damage, as measured in units of mean energy transferred per lattice atom.[2,9] The detailed correlation between defect structure and T_c depression is an open question, with several possibilities being considered.[1,2,5,8,12] In our case, the change of the superconducting parameters of V_3Si due to room-temperature proton irradiation will be treated as representative of irradiation damage in general.

While no comprehensive model exists, a good deal of work[17–24] has been done to calculate the fundamental parameters of the McMillan-Hopfield theory,[17,18] particularly the electron-phonon coupling constant λ. Only Ref. 23 applies explicitly to the changes expected on irradiation but the suggestion made there, namely, $\lambda/N(0)=$constant, is in agreement with the results of other work.[20–23] Our own results have allowed us to examine the extent to which this expectation, and others, are fulfilled for irradiated V_3Si.

II. EXPERIMENTAL METHOD

The samples used in the work were either polycrystals (4) or single crystal V_3Si (2). The crystals were cut by a spark cutter, and their final shape was a rectangular parallelepiped of dimensions roughly $1\times1\times10$ mm^3. All samples were cleaned in *CP*-4 solution[25] for 15–30 sec before measurement. This procedure removed the surface oxide layer and avoided problems of excessive contact resistance. Contact to the samples was made by four sharp spring loaded points[26] so that no soldering or annealing procedures were involved.

The irradiation was performed at the NASA Lewis Cyclotron which, for this study, accelerated protons to 37 MeV with a maximum beam current of 10 μA. The beam was focused with magnetic quadrupole lenses onto a carbon collimator containing a rectangular aperture about twice the size of the sample. A sample holder was mounted behind the collimator and the beam current passing through the collimator integrated to provide an on-line assessment of the fluence. The sample holder was milled from a solid aluminum disk with a 0.015-in. window which produced a 1.6-MeV loss for 37-MeV protons. Our samples were pressed against this window by phosphor bronze springs. Doubly deionized water at 80 psi overpressure circulated continuously around the sample so that its estimated maximum temperature rise during irradiation was less than 10 °C.

The total number of protons that had struck the sample was obtained by placing it at a measured distance from a Ge(Li) detector and determining the count rate of 320-keV photons from the 27.7-day half-life isotope, ^{51}Cr. This iostope is produced by a (p,n) reaction on ^{51}V which has a smoothly varying cross section for protons in the energy range of 23–37 MeV. The measured source strength was corrected back to the end of bombardment and the residual strength, i.e., the radioactivity remaining from previous irradiations, was subtracted to obtain the increment due to the last irradiation. The number of ^{51}Cr atoms produced during each bombardment was related to the proton fluence by using a factor obtained from an average of the (p,n) cross section (8.4 mb), the density of vanadium atoms, and the thickness of the sample. (The average cross section was measured in the energy interval 23–37 MeV using the usual stacked foil technique.) Errors in the proton fluence determination were mainly statistical together with uncertainties in the mass of the sample lost in the *CP*-4 etch. We estimate the combined error to be less than $\pm20\%$.

A 1-mm thickness of V_3Si decreases the proton energy from 35 to ~28 MeV with a constant spatial energy gradient. This produces a damage homogeneous to depth. Beam variation over the 1-mm width is in all cases negligible. Thus, the damage was distributed homogeneously in the two small dimensions of the sample. Uniformity of the proton bombardment along the long dimension of the sample was determined by moving the crystal in incremental steps across a 1-mm slit in a tantalum plate. The 320-keV peak intensity from a Ge(Li) detector positioned behind the slit showed the distribution of ^{51}Cr after irradiation to be uniform to within $\pm20\%$. However, we found that variations in the cyclotron beam distribution from run to run occurred in such a way that there was a tendency to achieve a significantly more uniform distribution of the damage. We are therefore confident that any total fluence was delivered with an overall uniformity along the sample length of better than $\pm20\%$.

For low-temperature measurement, the sample and thermometers were mounted on an oxygen-free high-conductivity copper (OFHC) copper plate inside a double-chamber cryostat. The outer can was evacuated while the inner can was filled with ^{4}He exchange gas and wound on the outside with a bifilar heater to control the temperature. The complete cryostat was immersed in a pumpable liquid-helium insert of a 2.5-in.-diameter 14-T superconducting magnet, whose field was measured with copper magnetoresistors calibrated by Hall probes. In the critical field measurements, the field was kept constant while the temperature was swept slowly up and down through the transition. The midpoint of the resistance transition was used to define the critical temperature. Resistivity and critical temperatures were measured with the above-mentioned four-point contacts by using both *dc* and *ac* methods with results being corrected for the mass loss in the cleaning process. Temperatures were measured using calibrated carbon glass thermometers[27] corrected for magnetoresistance.[28] These corrections were checked by us at 4.2 K. To cross-check temperatures we also used carbon and calibrated gallium arsenide diode thermometers. We carefully investigated the reproducibility of T_c measurements as function of exchange gas pressure, temperature sweep velocity, sample current, sample position in the cryostat, and long-term stability of the calibration against fixed points. The overall reproducibility was found to be within 0.1 K.

III. EXPERIMENTAL RESULTS

The irradiated samples included two single crystals which will be identified in the figures as Nos. 1SC

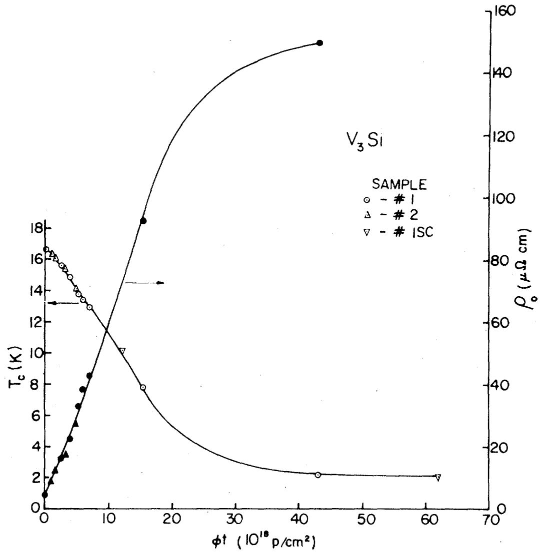

FIG. 1. Residual resistivity, ρ_0, and the critical temperature T_c, as function of the total proton fluence ϕt.

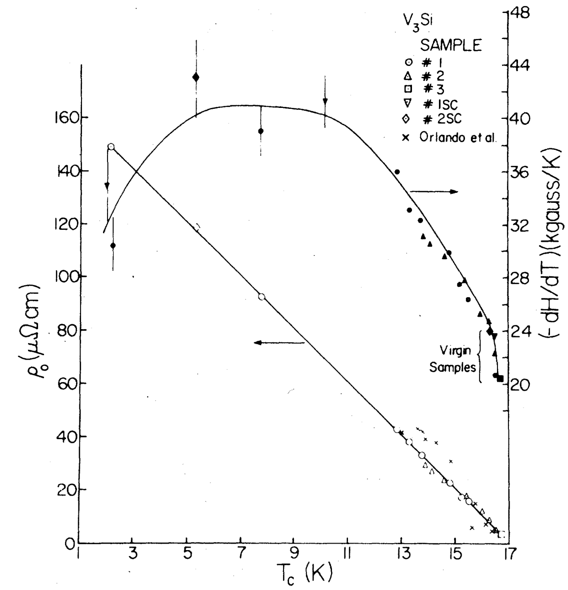

FIG. 3. Upper critical field slope $H_{c2}' = -(dH_{c2}/dT)_{T_c}$ and the residual resistivity ρ_0 as function of the critical temperature T_c.

and 2SC. Critical temperatures of all unirradiated samples were in the range $16.5 < T_c < 16.7$ K with transition widths (10–90%) from 0.08 to 0.14 K and residual resistivity ratios in the range 12 to 24. Figure 1 displays ρ_0 and T_c data versus fluence for the three most extensively investigated samples. Data at low fluences ($\phi t \simeq 10^{18}$ p/cm^2) was taken only for polycrystalline samples. As shown in Fig. 1, no threshold effect[5,9] is observed for these samples. This result is equivalent to that of Ref. 5, for polycrystalline V_3Si samples. A clear threshold has been observed in the literature[5] only in almost-defect-free single crystals. Thus, our result cannot rule out the existence of such an effect. A clear saturation at high influence is evident, comparable with the results of others.[1,8,29] The low-field portion of the critical field H_{c2} versus temperature data for one sample is shown in Fig. 2. (Most of our measure-

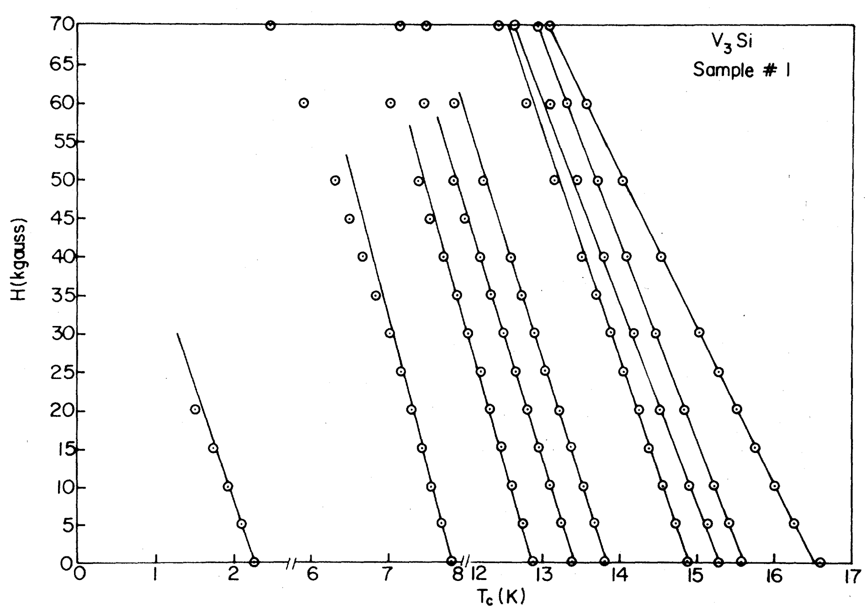

FIG. 2. Upper critical field H_{c2} as function of the temperature T at low fields for one sample.

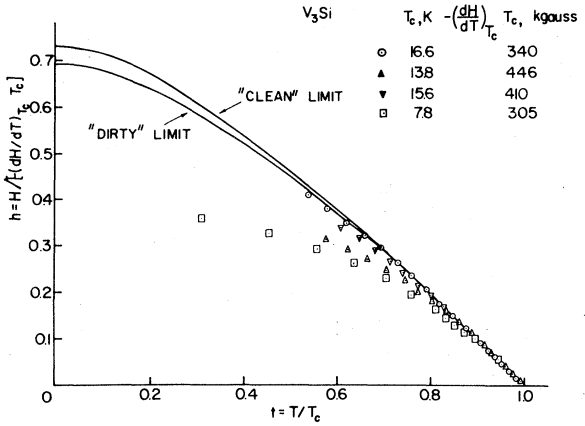

FIG. 4. Normalized upper critical field $h = H_{c2}/(T_c H_{c2}')$ as a function of reduced temperature $t = T/T_c$ for several samples. Theoretical results from Refs. 30 and 31.

ments were continued up to 14 T.) The data in this figure exhibit a linear region near T_c which was used to evaluate H_{c2}', the critical-field slope near T_c. These slopes are plotted against T_c in Fig. 3, together with our ρ_0 data and some results of the Orlando *et al.*[14] thin-film study of V_3Si. Our T_c-versus-ρ_0 results display a strikingly linear relationship that can be described by $\rho_0 = 171 - 10T_c$ where ρ_0 is in $\mu\Omega$ cm. This indicates that the maximum T_c for an ideal (nontransforming) sample would be 17 K.

The normalized upper critical field, $h = H_{c2}/(T_c H_{c2}')$ versus reduced temperature $t = T/T_c$ is shown in Fig. 4. Theoretical results[30,31] for isotropic type II superconductors with no paramagnetic limiting are shown on the same graph.

IV. DATA ANALYSIS

The electron phonon coupling parameter was estimated from the relation[32]

$$T_c = \frac{\bar{\omega}_{\log}}{1.2} \exp\left[\frac{-1.04(1+\lambda)}{\lambda - (1+0.62\lambda)\mu^*}\right] \quad (1)$$

using[18,19,32] $\bar{\omega}_{\log} = 0.56\Theta$ where Θ is a suitable Debye temperature[18,19,32] and $\mu^* = 0.10$. Only small changes in Θ result from irradiation[10] and they will be neglected here. Using a value of $\Theta = 420$ K, Eq. (1) then yields the λ values which are plotted against ρ_0 in Fig. 5. In order to estimate γ, the electronic specific-heat coefficient, we start with the general relation[12]

$$\gamma = \frac{2.2 \times 10^{-5} H_{c2}'}{\eta_{H_{c2}} \rho_0 (1 + 1.36 l/\xi_0^*)} , \quad (2)$$

where $\eta_{H_{c2}}$ is the strong coupling correction coefficient[33] for H_{c2} at T_c, ξ_0^* is the "dressed" coherence

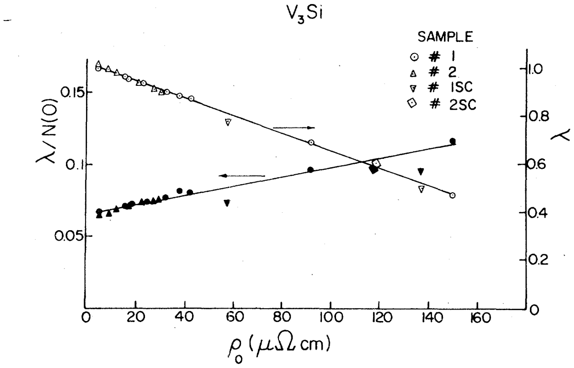

FIG. 5. Electron-phonon coupling constant, λ, and the ratio $\lambda/N(0)$, where $N(0)$ is the band density of states at the Fermi level, as a function of the residual resistivity ρ_0.

length in cm [$\xi_0^* = \xi_0/(1+\lambda)$], γ is in erg/cm^{3}K^2, ρ_0 in Ω cm, H_{c2}' is in G/K and l is the mean free path in cm. We next make the assumption that the Fermi-surface area remains constant on irradiation. This approximation has been used previously[12,14] and implies a constancy of $N(0)V_F$ and therefore $\rho_0 l$ where V_F is the Fermi velocity. A recent theoretical estimate[34] for some $A15$ materials confirms that $N(0)V_F$ is constant to within $\pm 10\%$ for $\rho_0 < 50$ $\mu\Omega$ cm. Using this approximation, we get

$$\gamma = \frac{3.73 \times 10^{-13} \rho_0}{(\rho_0 l)^2 T_c} \left[\left(1 + \frac{1.18 \times 10^8 T_c H_{c2}' (\rho_0 l)^2}{\eta_{H_{c2}} \rho_0^2} \right)^{1/2} - 1 \right] \quad (3)$$

The experimental value of $\rho_0 l$ for V_3Si was found by Muto *et al.*[35] by comparing critical field and specific-

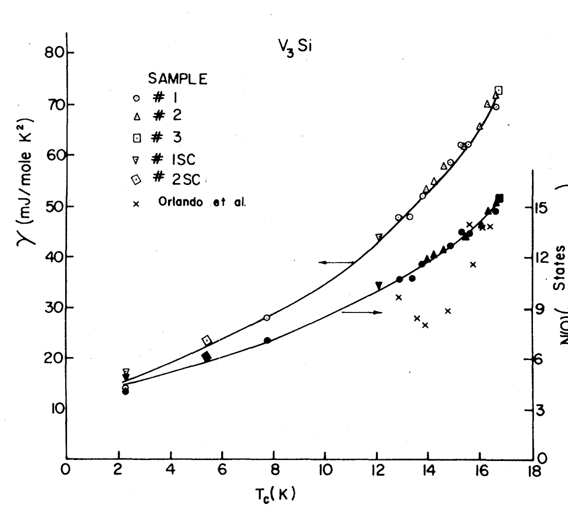

FIG. 6. Electronic specific-heat coefficient, γ, and the band density of states at the Fermi level, $N(0)$, as a function of the critical temperature T_c.

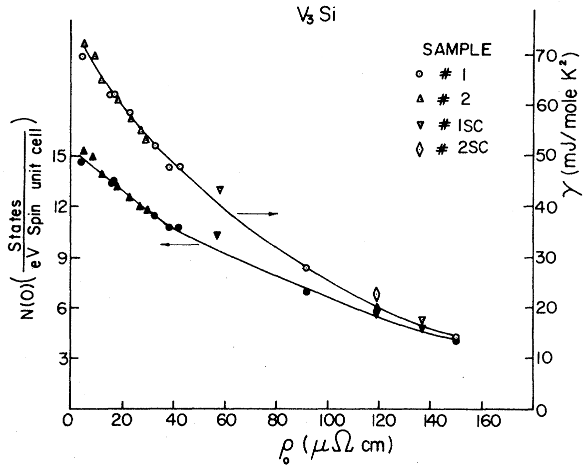

FIG. 7. Electronic specific-heat coefficient, γ, and the band density of states at the Fermi level, $N(0)$, as a function of the residual resistivity ρ_0.

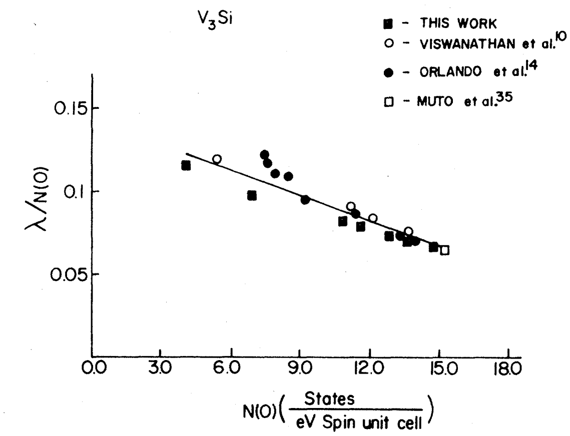

FIG. 9. The ratio $\lambda/N(0)$ vs $N(0)$. Additional data are from the specific heat on neutron irradiated crystals (Ref. 10) and from critical fields on quenched films (Ref. 14).

heat measurements on the same samples. Their result is $\rho_0 l = 5.45\times10^{-12}$ Ω cm^2, within 10% of the theoretical estimate.[34] Moreover, although not immediately obvious from Eq. (3), it turns out numerically that, for $\rho_0 > 50$ $\mu\Omega$ cm, variations in $\rho_0 l$ do not significantly effect our estimate of γ. The value of $\eta_{H_{c2}}$ for an unirradiated sample[14] is 1.05 and would be expected[33] to approach 1.0 on irradiation.

Results obtained for γ vs T_c and γ vs ρ_0 are given in Figs. 6 and 7. Using the values of γ and λ, we calculate $N(0)$ using

$$N(0)=\gamma/[\tfrac{2}{3}\pi^2 k_B^2(1+\lambda)] \quad , \tag{4}$$

where k_B is the Boltzmann constant.

The results of $N(0)$ vs T_c, ρ_0, and λ are given in Figs. 6, 7, and 8, respectively. We have also used

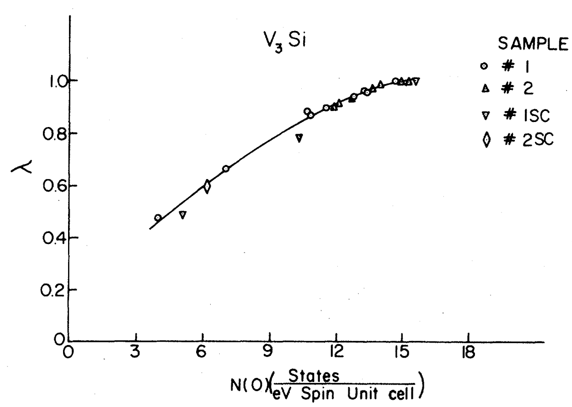

FIG. 8. Electron-phonon coupling constant, λ, as a function of $N(0)$.

the value of $N(0)$ to estimate the ratio $\lambda/N(0)$. This ratio is shown versus ρ_0 in Fig. 5 and versus $N(0)$ in Fig. 9.

V. DISCUSSION AND CONCLUSIONS

A. Critical-field data

Although some questions concerning the theory[30,31] have been raised recently,[36] it is clear qualitatively that irradiation acts so as to increase the effective paramagnetic limitation on the critical field. Quantitatively, we found that the Werthamer, Helfand, and Hohenberg theory[30] gives a reasonable fit to our $h(t)$ data for all values of the slope H'_{c2}. However, this agreement could only be secured if a renormalized[37] Maki parameter $\alpha^* = \alpha\eta_{H_c}(0)(1+\lambda)$ is used where α is the bare Maki parameter. A value of $\eta_{H_c}(0)=1.11$ was taken for unirradiated samples, decreasing[33] toward 1.0 with irradiation. Using the bare Maki parameter, the theoretical result gives too low a paramagnetic limitation for any value of the spin-orbit parameter[30]

B. Density of states $N(0)$

A striking consequence of irradiation is the marked drop of $N(0)$ as T_c is reduced (Fig. 6) and ρ_0 increased (Fig. 7). The results of Orlando *et al.*[14] are in broad agreement with ours but exhibit substantially more scatter and are confined to a much narrower range of the experimental parameters. The sharp reduction of $N(0)$, by almost a factor of 4, points to the existence of a very sharp peak in the density of states of the starting material.

C. Electron phonon interaction

From Fig. 8, it is clear that $\lambda/N(0)$ is *not* constant, in contradiction to the assumption made in other work[1,12,20] and the implication of the model discussed in Ref. 23. Our experimental $\lambda/N(0)$ results are plotted in Fig. 9 in a form which shows that an empirical relation of the type $\lambda = AN(0) - BN(0)^2$ describes the data quite well. Other available data plotted there are also not inconsistent with our result. Using McMillan's[17] approximation, one obtains

$$\lambda = \frac{N(0)\,\langle I^2\rangle}{M\,\langle\omega^2\rangle} , \tag{5}$$

where $\langle\omega^2\rangle$ is some average over the phonon frequencies and $\langle I^2\rangle$ is the average of the electron-phonon interaction over the Fermi surface. Our result shows that $\langle I^2\rangle/\langle\omega^2\rangle$ increases with irradiation since the atomic mass M is unaltered. In the simplest situation[18,19] $\langle\omega^2\rangle$ is proportional to Θ^2 and, recalling that we are assuming that Θ itself stays constant, this in turn implies a marked increase in $\langle I^2\rangle$. A large ($\sim 70\%$) increase in $\langle\omega^2\rangle$ without any change in Θ would be very difficult to explain. We are therefore obliged to conclude that some marked increase in $\langle I^2\rangle$ occurs as $N(0)$ decreases. Any theoretical relation between $\langle I^2\rangle$ and $N(0)$ will necessarily depend on a number of assumptions. A new calculation[24] is apparently in at least qualitative accord with our result but it will be interesting to see to what extent theory can quantitatively account for data of this sort on V_3Si and the other $A15$'s.

ACKNOWLEDGMENTS

We would like to thank Dr. John A. Woollam for helpful discussions and for the loan of cryogenic apparatus. We would also like to thank Dr. J. H. Wernick for supplying one of the single crystals used in this investigation. The work at CWRU was supported by NSF Grants No. GH-34409 and No. DMR-75-18642.

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