PHYSICAL REVIEW B VOLUME 15, NUMBER 5 1 MARCH 1977

Anomalous electrical resistivity and defects in A-15 compounds

L. R. Testardi, J. M. Poate, and H. J. Levinstein
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 2 August 1976)

The temperature dependence of the electrical resistivity ρ of Nb-Ge, V_3Si, V_3Ge, and Nb is reported for a variety of samples produced with differing chemical composition (for Nb-Ge), preparation conditions, and with varying amounts of ^{4}He-induced defects. The great susceptibility of the A-15 structure to defect formation and its profound effects on the physical behavior are shown. The resistance-ratio–T_c correlation previously reported for Nb-Ge is found in V_3Si and V_3Ge. Residual resistivities increase far more rapidly with ^{4}He-induced defects in the A-15's than in Nb, and at least for Nb_3Ge, saturate at the highly disordered state where the minimum T_c occurs. Decreasing T_c, no matter how achieved, is accompanied by not only the loss of the Woodard and Cody anomaly in $\rho(T)$ but the loss of almost all the thermal resistivity (electron-phonon interaction) as well. The temperature dependence and the magnitude of ρ are compared with predictions and other published values and some unexpected correlations with T_c are found. The data indicate a defect with universal behavior in the A-15's, and of considerable consequence to the superconducting and normal-state behavior.

I. INTRODUCTION

One of the most important problems in the study of high-T_c superconductors is to learn what aspect of the chemistry or structure of A-15 compounds is crucial for achieving the high-superconducting transition temperatures as well as the numerous anomalies associated with these materials. Over the years, and from many experiments, it has come to be accepted that the crucial "materials" parameter is the presence of exact chemical stoichiometry and/or the absence of a peculiarly detrimental defect generally thought to be simple antisite disorder. In a recent study[1] of A-15 Nb-Ge alloys it was shown that although T_c does vary with chemical composition, it does not exhibit the very critical dependence on stoichiometry which has sometimes been expected.

Because of the considerable metallurgical flexibility now possible in thin films, and, as shown by Sweedler and colleagues[2] and others,[3,4] the universally large reductions in T_c obtained with radiation damage, it is now possible to test the superconducting as well as the normal-state properties over wide variations in the microstate of the materials. In the present study, we report the anomalous electrical resistivity of some A-15 materials and its variations with large changes in T_c brought about in several ways.

Woodard and Cody[5] were the first to point out that a material exhibiting high-temperature superconductivity also showed an anomalous temperature dependence of its normal-state electrical resistivity ρ. [The first reported observations of $\rho(T)$ were by Sarachik *et al.*[7]]. Instead of the approximately linear temperature dependence for ρ (for T above $\sim\frac{1}{5}$ the Debye temperature) usually found in most metals, these authors found considerable negative curvature in $\rho(T)$ for Nb_3Sn between ~400 and 50 K with an inflection point and positive curvature at lower T. This general behavior was found in many of the other high-T_c A-15 structure superconductors,[6-8] and more recently Fisk and Lawson[9] showed its occurrence in a wider variety of materials, again having relatively high-superconducting transition temperatures.

At least for the A-15 compounds the electrical resistivity is one of a number of physical properties with anomalous temperature dependences of the normal-state behavior.[10] We will summarize below a number of the theoretical models and conjectures which have been offered to explain this result. The ultimate goal of many (though not all) of these treatments is to find the anomalous resistivity as another predictable consequence of the structural instability inherent in many of these A-15 compounds. Furthermore, such treatments can at least help clarify a qualitative picture of how the high-temperature superconductivity relates to the structural instability.

It will be the major conclusion of this work that there is a qualitatively universal behavior in the electrical resistivity of diverse samples of these materials, and that further evidence suggests this behavior is due to the defects which have a common and sometimes profound effect on the physical behavior. These defects may be as much a consequence of the structural instability as is the high T_c; their effect on the superconductivity is demonstrably no less crucial.

TABLE I. Electrical properties of films.

Sample (No.)	Composition[a]	Preparation conditions[b]	T_c[c] (K)	ρ(300 K)[d] ($\mu\Omega$ cm)	$\rho(T_c)$[e] ($\mu\Omega$ cm)	ρ(300 K)/$\rho(T_c)$
Nb-Ge (1)	3/1	Opt T_D	23.0–22.0	90	36	2.5
Nb-Ge (2)	2.7/1	Nonopt T_D	21.5–19.7	91	52	1.75
Nb-Ge (3)	3/1	Nonopt T_D	13–11.5	96	73	1.32
Nb-Ge (4)	4.1/1	Nonopt T_D	12.5–11.2	100	89	1.12
Nb-Ge (5)	5.5/1	Opt T_D	9–6.5	120	108	1.11
Nb-Ge (6)	3/1	Opt T_D+5×10^{16} cm^{-2} ^{4}He	6–4.9	133	131	1.02
Nb-Ge (7)	3/1	Nonopt T_D	<4.2	190	190	1.00
V-Si (1)	~3/1	Opt T_D	16.7–16.1	88	5.0	17.6
V-Si (2)	~3/1	Opt T_D	12–10	108	65	1.66
V-Si (3)	~3/1	Opt T_D+1.3×10^{17} cm^{-2} ^{4}He	~5 – <4.2	125	122	1.02
V-Si (4)	~3/1	Nonopt T_D	13.6–12.2	255	126	2.02
V-Si (5)	~3/1	Nonopt T_D	<4.2	1175	1120	1.05
V-Ge (1)	~3/1	Opt T_D	7–6	80	6.0	13.3
V-Ge (2)	~3/1	Opt T_D+5×10^{16} cm^{-2} ^{4}He	4.8–4.2	123	86	1.43
V-Ge (3)	~3/1	Opt T_D+1×10^{17} cm^{-2} ^{4}He	<4.2	142	125	1.14
V-Ge (4)	~3/1	Nonopt T_D	<4.2	925	685	1.35
Nb (1)	•••	Opt T_D (~750 °C ± 100 °C)	9.3–9.1	15	0.15	100
Nb (2)	•••	T_D~ 550 °C	9.3–9.2	16	0.98	16.3
Nb (3)	•••	Opt T_D+5×10^{16} cm^{-2} ^{4}He	9.3–9.1	18	2.4	7.5
Nb (4)	•••	T_D~ 350 °C	9.1–8.9	80	35	2.29
Nb (5)	•••	T_D ~ 50 °C	8.7–8.6	105	43	2.44

[a] (1), compositions were determined to ~±5% by Rutherford backscattering.

[b] (2), for $A-15$ materials deposition conditions are called Opt (Nonopt) if T_c is less (greater) than 1 K of the highest values obtained for that composition. Nonoptimum conditions were generally achieved with deposition temperatures T_D~ 20 °C – 80 °C below the optimum value. For Nb, lower T_D's affect the resistance ratio considerably more than T_c.

[c] (3), T_c's are onset and completion temperatures (±0.2 K) of resistive transition.

[d] (4), absolute ρ's are uncertain to ~25% due mainly to film thickness uncertainty but temperature dependences are correct to ~5%.

II. EXPERIMENTAL

Samples of Nb, Nb_xGe ($x=2.7$ to 5.5) V_3Si, and V_3Ge were obtained by getter sputtering[11] onto hot Al_2O_3 substrates. Film thickness were generally ~2500–4000 Å except for one Nb film (see below) whose thickness was ~8000 Å. For Nb-Ge, a wide range in chemical composition (still yielding predominantly A-15 phase) was studied. For all films chemical composition was determined by Rutherford backscattering to an accuracy of ~5%. The preparation and analysis methods of these films has been discussed in greater detail elsewhere.[1]

In addition to varying the chemical composition (for Nb-Ge) large variations in T_c were achieved in all A-15 samples by nonoptimum growth conditions and by ^{4}He-particle radiation damage.[4] Nonoptimum growth conditions were generally obtained with deposition temperatures ~20 to 80 °C (occasionally greater) below the optimum value. Radiation damage studies were made in samples initially prepared under optimum as well as nonoptimum conditions.

Electrical resistivity measurements were made by standard four-probe ac methods with current densities $\lesssim 1$ A/cm^2. Continuous recording of ρ vs T from 300 to 4.2 K was achieved using a linearized output of a silicon-diode thermometer. Absolute resistivities are uncertain to ~25% due mainly to film thickness uncertainty[1] (and nonuniformity) but temperature dependences are accurate to ~5%. Temperature measurements are accurate to ~0.2 K below 30 K and, to ~1 K at the higher temperatures.

Table I summarizes the composition, preparation conditions, and electrical properties of some of the samples studied. These samples exhibit typical behavior for the conditions indicated and their results will be discussed at greater length below.

III. RESULTS AND DISCUSSION

A. Resistance-ratio correlations

Recently, a correlation between the electrical-resistance ratio ρ(300 K)/ρ(25 K) and T_c has been reported in Nb-Ge films.[1] The correlation was observed over the wide stoichiometric range Nb/Ge 2.5–5.5, where the A-15 phase is obtained,[12] and for wide variations in growth conditions (film thickness, sputtering voltage, argon pressure,

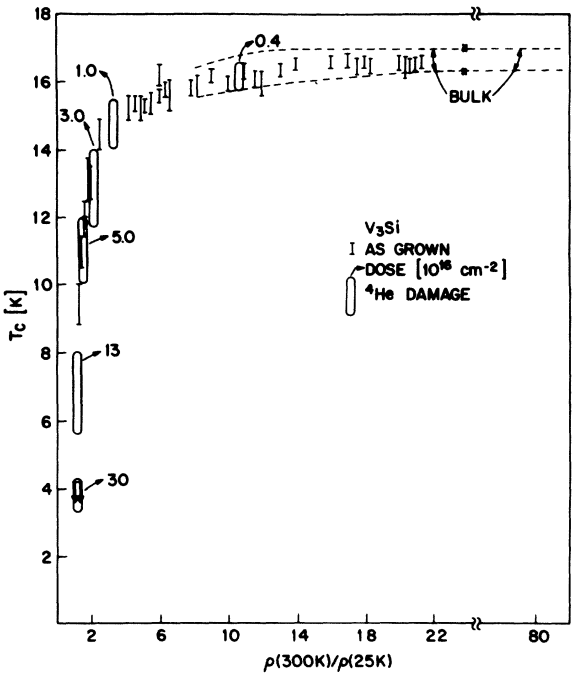

FIG. 1. T_c vs resistance ratio for a variety of V_3Si films. No measurements were made below 4.2 K.

and deposition temperature). This result, together with the failure to find a critical-T_c–composition dependence, led to the suggestion that defects with some universal character, were primarily responsible for the difficulty in achieving the optimum superconducting properties. Evidence for this suggestion came in subsequent studies[4] where it was shown that the resistance-ratio–T_c correlation could be reproduced at constant chemical composition by introducing defects only (with ^{4}He particles which do not stop in the film) in initially high-T_c samples.

Figures 1 and 2 show that T_c–resistance-ratio correlations occur in V_3Si and V_3Ge as well. The various T_c's for these data were obtained mainly by variations in the growth procedure with changes in stoichiometry limited to about 10% in V/Si or V/Ge ratios about the value 3.0. These correlations are, in fact, quite similar to that found for Nb-Ge. The principle difference is that for these compounds one can obtain resistance ratios in the sputtered film up to ~20 which compares favorably with many bulk single-crystal values.

Indeed, for resistance ratios ~1 to 3, where all data for Nb-Ge fell, the correlation for V_3Si looks quite similar to that for Nb-Ge. For V_3Si and V_3Ge the limiting T_c's occur for resistance ratios $\gtrsim 10$. If this behavior also applies to Nb-Ge, where the highest resistance ratios were ~2.5-3, one would estimate that an increase in T_c ~1-2 degrees above the highest yet reported could accompany a marked improvement in sample perfection.

The significance of these correlations—that T_c's can be strongly influenced by a defect with universal character—is further supported by ^{4}He radiation-damage studies. These results,[13] given in Figs. 1 and 2 show that the T_c–resistance-ratio correlation for V_3Si and V_3Ge (like Nb-Ge and Nb-Sn)[13] can be reproduced in high-T_c samples by the introduction of controlled amounts of defects only while holding the chemical composition constant.

Before any further discussion of the nature or the roll of the defects, we will give several other examples of how intentionally introduced defects can simulate the behavior of as-grown (nonoptimum) A-15 samples.

B. Defect contributions to ρ and the residual resistivity

The resistance ratio is a standard and convenient way to compare sample qualities. Variations in

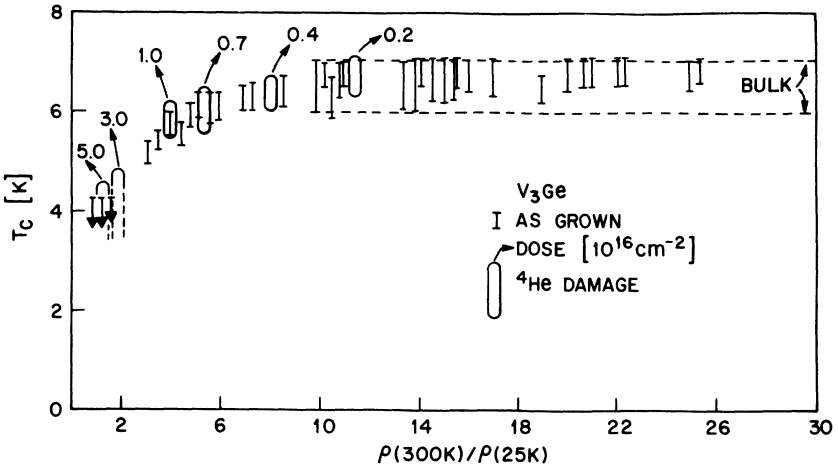

FIG. 2. T_c vs resistance ratio for a variety of V_3Ge films. No measurements were made below 4.2 K.

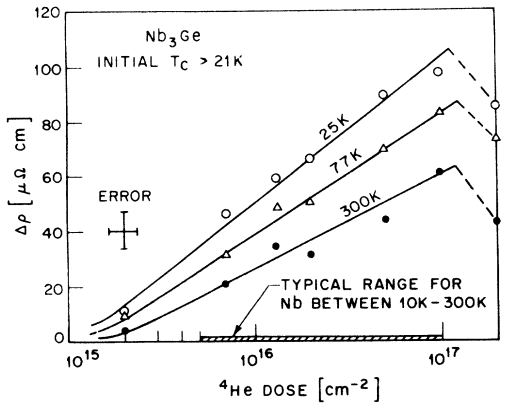

FIG. 3. Increase in resitivity $\Delta\rho$ vs ^{4}He dose at 25, 77, and 300 K for high-T_c Nb_3Ge.

this number generally imply change in the residual resistivity ρ_0 but much less in the thermal resistivity ρ_{th}. Although we will shortly show that this behavior—Matthiessen's rule—fails for the A-15 compounds, we discuss first the increase in residual resistivity with ^{4}He radiation damage.

Figure 3 shows the increase in resistivity at 25, 77, and 300 K with (~2-MeV) ^{4}He dose (at 300 K) for a series of samples of high-T_c Nb_3Ge similar to Nb-Ge No. 1 of Table I. Previous studies[4] have shown that ^{4}He doses up to ~2×10^{17} cm^{-2} in this material cause the lattice parameter to increase by up to ~1% and the T_c to decrease by ~18 to 19 K reaching a saturation value (independent of further dose) of ~3.5 K at ~1×10^{17}-cm^{-2} ^{4}He.

Figure 3 shows that an increase in residual resistivity (corresponding approximately to the 25-K data) accompanies the decrease in T_c as the ^{4}He dose increases. The rate of increase in ρ_0 at low dose appears more rapid than that for T_c; however, this conclusion cannot be inferred reliably because of the large uncertainty in this comparison of absolute resistivities.

Note that the increase in ρ_0 with dose is arrested at ~1×10^{17}-cm^{-2} ^{4}He particles. This is approximately the dose where the reduction in T_c is also arrested. Thus, the saturated T_c state is accompanied by a maximum or, in view of the error, a saturated value of ρ_0. This value of ρ_0, furthermore, is ~100–150 $\mu\Omega$ cm which, in the simplest approximation, indicates an electron mean free path of about several atomic separations. The saturated T_c and ρ_0 state, therefore, is also a state of approximate maximum disorder for electron scattering. This is further corroborated by x-ray measurements which show the considerable weakening of all lines (e.g., loss of long-range order) except those at low angles for these irradiated films.

Figure 3 also shows the increase in ρ with ^{4}He dose at all T between 10 and 300 K for Nb films. Note that for this "typcial" transition metal, these doses cause an increase in ρ~1–2 $\mu\Omega$ cm and a decrease in T_c~0.1–0.2 K—both almost two orders of magnitude less than that for A-15 Nb-Ge. Clearly, defects in the A-15's are more easily made and/or they are of far greater significance to the physical behavior.

Finally, Fig. 3 also shows that Matthiessen's rule does not apply to A-15 NbGe. (It does approximately work for Nb—see below.) The increase in resistivity due to defects is not temperature independent but is almost twice as large at low temperatures as at room temperature. This behavior, of greater significance to superconductivity, is discussed in Sec. III C.

Figure 4 shows the increase in resistivity for A-15 Nb-Ge films which have only moderate T_c's ~10 to 14 K, due to either nonstoichiometry, nonoptimum preparation, or ^{4}He-particle damage. Their physical properties are similar to Nb-Ge Nos. 3 to 6 in Table I. Note that at low doses (<1.5×10^{16} cm^{-2}), $\Delta\rho$ is considerably less than that obtained for the high-T_c samples. At the higher doses, however, $\Delta\rho$ and ρ increase rapidly, approaching values comparable to those for the initially high-T_c samples. This shows an extension of the "equivalent-defect hypothesis" proposed earlier.[4] Samples with nonoptimum T_c's, according to this suggestion, have defects comparable to that introduced by the ^{4}He dose which produces the same final T_c in an initially optimum T_c film.

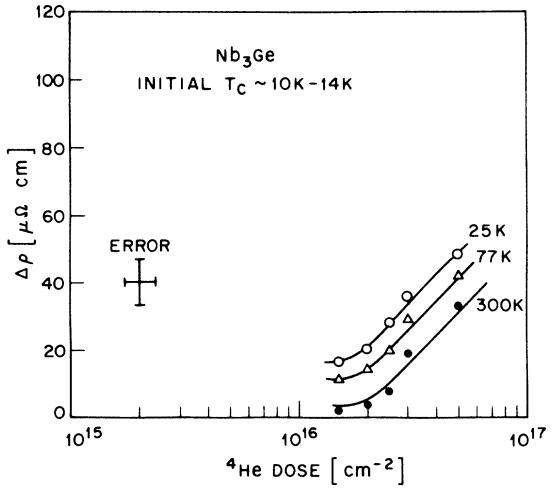

FIG. 4. Increase in resistivity $\Delta\rho$ vs ^{4}He dose at 25, 77, and 300 K for moderate-T_c Nb_3Ge.

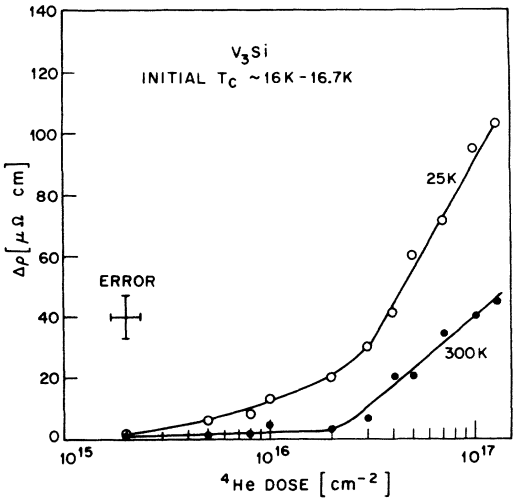

FIG. 5. Increase in resistivity $\Delta\rho$ vs ^{4}He dose for V_3Si.

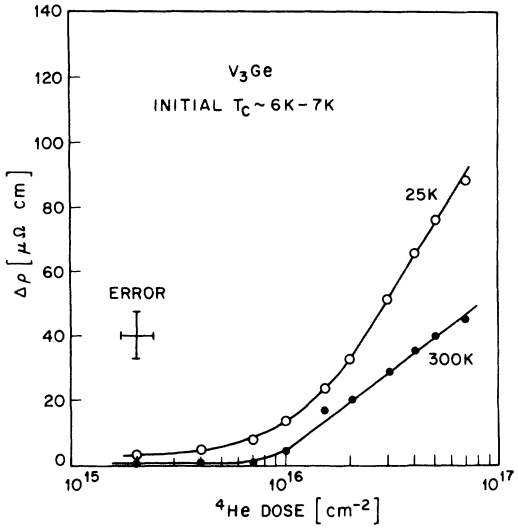

FIG. 6. Increase in resistivity $\Delta\rho$ vs ^{4}He dose for V_3Ge.

According to prior studies,[4] a ^{4}He dose ~1.5×10^{16} cm^{-2} should produce defects of comparable effect to those occurring in a 12-K film obtained by non-optimum preparation. One would further not expect a significant increase in defects or ρ with irradiation until that "equivalent" dose is achieved. Beyond this, additional dose will lead to changes in T_c and ρ similar to those found in high-T_c films. A comparison of Figs. 3 and 4 and the data of Table I show that this simple expectation is at least qualitatively confirmed.

Figures 5 and 6 show $\Delta\rho$ versus dose for near-optimum-T_c V_3Si and V_3Ge. The behavior is quantitatively similar to that in Nb-Ge, again showing the universal behavior of these defects among various A-15 compounds. The main qualitative difference is that a higher dose is required in V_3Si and V_3Ge before the rapid increase in $\Delta\rho$ occurs. This higher dose to achieve comparable degradation is also evident in the T_c behavior.[13] It no doubt reflects the fact that V_3Si and V_3Ge are more stable compounds and less susceptible to defect formation than A-15 Nb-Ge.

C. Temperature dependence of the resistivity

The temperature dependence of ρ between 4 and 300 K for five samples of Nb are shown in Fig. 7. (Sample descriptions are given in Table I.) Sample 1 has ρ(300 K) = 15 $\mu\Omega$ cm in good agreement with the standard bulk value, and a resistance ratio ρ(300 K)/ρ(10 K) = 100. The film thickness, in this case, was increased to ~8000 Å to minimize (though perhaps not entirely eliminate) surface scattering effects due to the long electronic mean free path. The large resistance ratios for Nb, V_3Si, and V_3Ge show that the getter-sputtering process is inherently capable of producing good quality films with small impurity concentrations. The low resistance ratios (< 3) for Nb_3Ge are due, therefore, to a comparatively large amount of defects naturally occurring in this compound and not impurities as further demonstrated in Ref. 1.

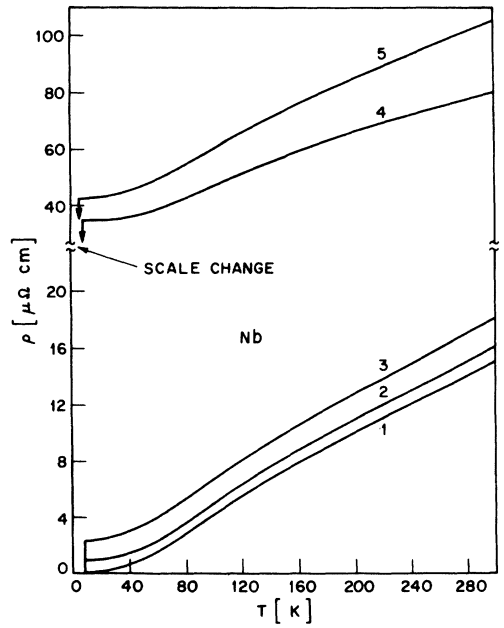

FIG. 7. The temperature dependence of the electrical resistivity for Nb films. See Table I for the sample descriptions.

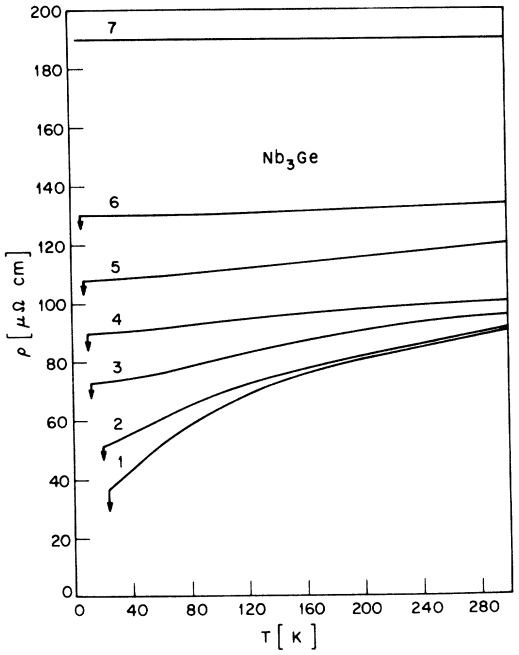

FIG. 8. Temperature dependence of the electrical resistivity for Nb_3Ge films. See Table I for the sample descriptions.

Nb sample Nos. 2 and 3 were obtained by nonoptimum preparation, and by ^{4}He-particle damage, respectively. The ^{4}He dose which resulted in $\Delta\rho_0 \sim 100$ $\mu\Omega$ cm and $\Delta T_c \sim 15$ K in Nb_3Ge causes, in Nb, $\Delta\rho_0 \sim 2$ $\mu\Omega$ cm and $\Delta T_c \sim 0(\pm 0.2)$ K. Since the average nuclear mass and charge (which defines the energy transferred to the recoiling nucleus) is not very different between these substances the great disparity in damage effects must result from the susceptibility of the A-15 structure to some defect formation.

Nb sample No. 1 also exhibits a slight (anomalous) negative curvature in $\rho(T)$ generally seen in this element. Note, however, from sample Nos. 2 and 3 that when defects are introduced the increase in ρ at all T is approximately equal to the increase in ρ_0. Thus Matthiessen's rule roughly applies to Nb.

A dilemma which occurs in the interpretation of the thin film resistivities is also illustrated in Fig. 7. Films prepared to very low deposition temperature (Nb Nos. 4 and 5) tend to have comparatively very high values of the residual as well as the thermal part of the electrical resistivities but still maintaining reasonable values of resistance ratios and T_c. As we will show below for the A-15 compounds, these values of ρ_0 and ρ_{th} can sometimes become unusually large for a metal and a convincing explanation is not available. In any event, it is just this behavior (and not only the convenience of measurement) which allows T_c in these cases to correlate far better with resistance ratios than with absolute resistivities.

Figure 8 shows $\rho(T)$ for seven Nb-Ge films with a range in T_c's of almost 20 K. (See Table I for descriptions.)[14] The sample for the lowest curve had a resistive $T_c \sim 23$ to 22 K and clearly shows the anomalous temperature dependence of resistivity (large negative curvature plus an inflection point) first noted by Woodard and Cody[5] in an A-15 compound. The wide range in T_c's for these samples was obtained, again, by nonstoichiometry, nonoptimum preparation, and radiation defect formation in otherwise good samples. Since the curves are ordered upwards by decreasing T_c it is evident that, not only does the Woodard and Cody anomaly disappear as the T_c is lowered, but that its disappearance is correlated in a gradual manner with T_c and is at least grossly independent of how the lowered T_c's have been achieved. Figures 9 and 10 show the behavior found in V_3Si and V_3Ge. Note, again, (i) the quantitative similarities in $\rho(T)$ and its variation with T_c, and (ii) the very high resistivities, with resistance ratios greater than one, found with low-deposition temperatures. Although not too evident in Figs. 8 and 9, high-resistivity samples with resistance ratios ~1 often have resistance minima between 4–100 K. This is a somewhat common occurrence for the very disordered alloy films of our studies.

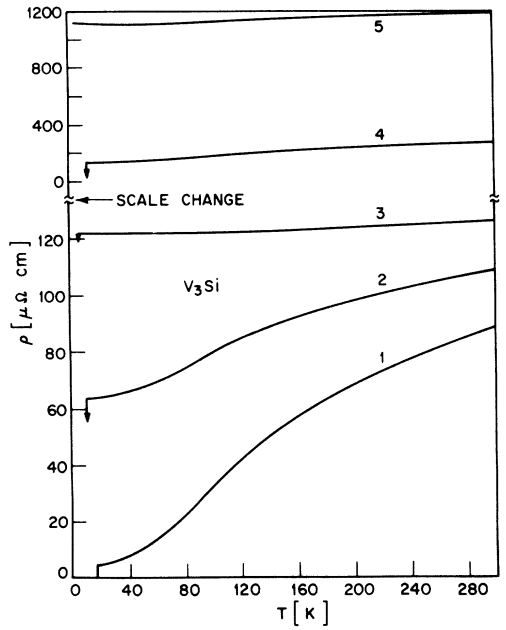

FIG. 9. Temperature dependence of the electrical resistivity for V_3Si films. See Table I for the sample descriptions.

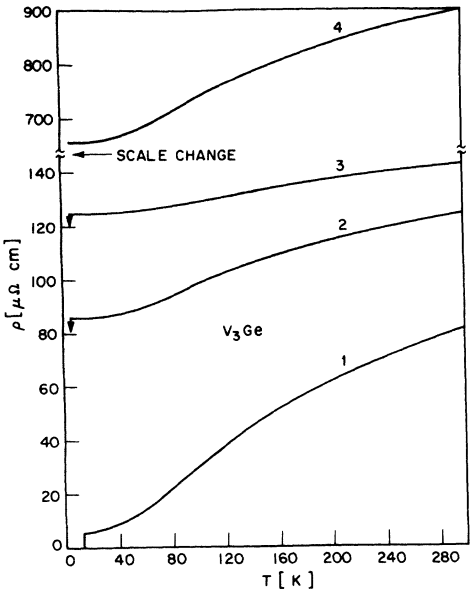

FIG. 10. Temperature dependence of the electrical resistivity for V_3Ge films. See Table I for the sample descriptions.

The actual temperature dependence of the resistivity has been the subject of several model calculations and conjectures. For a simple metal the temperature dependence of the electrical resistivity is given by the Bloch-Grüneisen theory. This expected behavior is shown in Fig. 11 where ρ vs T is plotted with both parameters normalized to their values at the Debye temperature Θ. At all but the lowest temperatures much of the temperature dependence of the resistivity arises because the scattering cross section for the electrons is (largely) proportional to the mean square thermal motion of the atoms $u^2(T)$ (proportional to T at high T). The comparison is shown in Fig. 11 which also gives $u^2(T)/u^2(\Theta)$. The ρ/u^2 proportionality factor, which depends mainly on the electronphonon interaction for transport processes, is not evaluated in the theory but assumed to be independent of temperature.

Woodard and Cody found that the thermal part of the resistivity for Nb_3Sn did not behave according to the Bloch-Grüneisen theory but could be fitted over the range 18–850 K by the expression

$$\rho_{th} = \rho_1 T + \rho_2 e^{-T_0/T} \quad (1)$$

(see Table II for the coefficients). A theory of sd scattering given by Wilson does predict behavior of the form of Eq. (1) but Woodard and Cody found numerical inconsistencies in the simplest test of this theory. Cohen, Cody, and Halloran[15] later showed that if the theory is applied to a system with sharp structure in the density of states near the Fermi level it was possible to calculate the observed behavior using several adjustable parameters which, in turn, would successfully predict other important properties. In this theory T_0 (~85 K for Nb_3Sn) in Eq. (1) is a measure of the Fermi level relative to the position of the density-of-states singularity. Milewits, Williamson, and Taub[8] have recently shown Eq. (1) to describe the resistivity of V_3Si (see Table II for the parameters) but interpret T_0 as the energy of [100]TA phonons for both Nb_3Sn and V_3Si.

Testardi and Bateman[16] suggested, on the other hand, that the anomalous $\rho(T)$ could result from the mode softening [i.e., anomalous $u^2(T)$] in these materials. Using the low-frequency-sound velocity results, which should overestimate the anomaly, a difference ~25% at 50 K in ρ_{th} for transforming and nontransforming crystals was estimated. Taub and Williamson[17] have reported no difference experimentally to within 6%. A further discussion of the effects of anharmonicity (related to the mode softening) has been given,[18] and recently Allen *et al.*[19] obtained semiquantitative agreement in a calculation of the anomalous $\rho(T)$ in which the effects of anharmonicity were included.

Equation (1) provides not only a test of some theories but also a convenient way to describe and compare the resistivity anomalies. We have

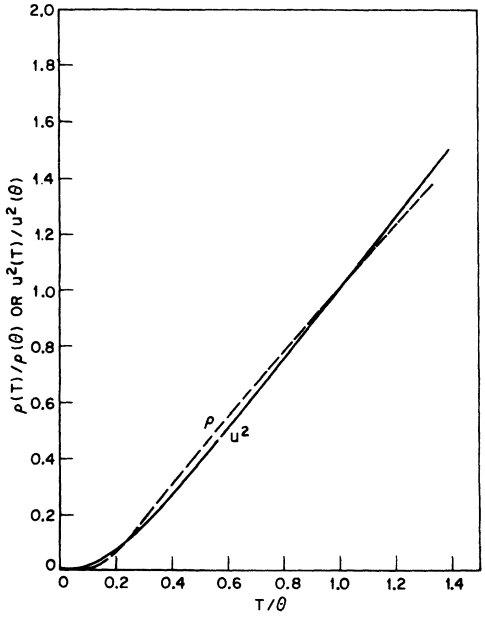

FIG. 11. Electrical resistivity from the Grüneisen-Bloch theory and mean-square thermal motion from Debye theory vs T/Θ. Both ordinate quantities are normalized to their value at the Debye temperature Θ.

TABLE II. Parameters for Eq. (1).

Material (No.)	T_c (K)	ρ_1 ($10^{-2}\mu\Omega$ cm)	ρ_2 ($\mu\Omega$ cm)	T_0 (K)
Nb_3Sn [a]	~18	4.6	74.7	85
V_3Si [b]	~15–17	5.7–5.8	72–97	163–180
V_3Si (1) [c]	~16.4	~5	~120	170
V_3Si (2) [d]	~11	~5.4	~53	140
V_3Ge	~7	[similar to V_3Si(1)]		
Nb_3Ge (1)	~22.5	~3.8	~57	80
Nb_3Ge (3)	~12	~2.2	~28	160
$Nb_{5.5}Ge$ (5)	~7.5	~1.6	~16	240
Nb (1)	~9.2	~0.8	~25	210

[a] Reference 4.

[b] Reference 8.

[c] Temperature range (and accuracy) for the parameter fits are 18–850 K (~1%?) for Woodward and Cody, 17–50 K (4%–7%) for Milewits *et al.*, and 30–300 K (~25% for ρ_2) for the present data.

[d] Characterization for samples of present study are given in Table I.

fit our ρ_{th} to Eq. (1) for a number of samples of Nb_3Ge, V_3Si, and V_3Ge having a wide range in T_c. The results, which generally describe ρ_{th} to ~5% ± 0.5 $\mu\Omega$ cm between 30 and 300 K, are shown in Table II along with the coefficients obtained by Woodard and Cody[14] for Nb_3Sn and Milewits *et al.*[8] for V_3Si. In view of the differing temperature ranges of the fits and uncertainties (see Table II notes), only the broad trends should be noted. The following observations summarize the comparisons. (i) High-T_c Nb_3Sn and Nb_3Ge are qualitatively similar. (ii) Lower T_c's in Nb_3Ge are accompanied by smaller values for both the linear and exponential coefficients. For V_3Si this is also true for the exponential coefficient; however, for the linear coefficient the uncertainty is so large in this case (perhaps a factor of 2) that no conclusion can be drawn. (iii) The value of T_0 (which is twice the inflection temperature for ρ) decreases slightly in V_3Si but increases roughly proportional to $1/T_c$ in Nb_3Ge as their T_c's are lowered. The last observation is significant in showing that T_0 is capable of significant variation but does not behave in a universal manner for the A-15's. Within the Cohen, Cody and Halloran[15] model one might expect a variation in T_0 (Fermi level) with chemical composition. However, as noted above, the changes in $\rho(T)$ (and T_0) correlate roughly with T_c whether the latter is lowered by nonstoichiometry or by defects (at fixed composition). The data clearly show the decisive role which defects may play in the anomalous resistivity.

The great similarity in $\rho(T)$ for V_3Si (T_c~17 K) and V_3Ge (T_c~6 K), first observed by Sarachick *et al.*,[7] show that high T_c's do not always accompany the anomalous resistivity. Although several V_3Ge films with T_c onsets ~8 K were obtained in this study there is, as yet, no indication that significantly higher T_c's (~15 K) can be obtained. This compound, generally neglected by most workers because of its low T_c, remains one of the great puzzles among the A-15 superconductors.

A final comment on the temperature dependence of ρ comes from a recent model of Gor'kov[20] for A-15 materials who suggested that the resistivity should be proportional to $\ln T$. (This behavior results from a singularity in the electron density of states which, in the mathematical treatment, yields $\ln T$ dependence for a number of properties.) Figures 12 and 13 show the Gor'kov suggestion tested, and reasonably confirmed in Nb-Ge and V_3Si. Furthermore, the $\ln T$ behavior is found not just for the high-T_c material but over a wide range in T_c which can be produced, again, by nonstoichiometry, nonoptimum growth, or intentional defects. (The discrepancy at low-T results because $\ln T$ cannot be fit through an inflection point and this limits the validity of the test, particularly for V_3Si.) Somewhat unexpectedly, the prefactor in such a $\ln T$ fit is found to be roughly proportional to T_c in both compounds. Gor'kov did not theoretically derive the resistivity, but it is possible that in such a treatment may lie a quantitative connection with the superconductivity.

The failure of the A-15 compounds to follow Matthiessen's rule suggests that defects have a strong influence on the electron-phonon interaction. This can be seen in the data of Lutz *et al.*[14] and in Fig. 14 which gives the variation of thermal part of the resistivity at 300 K with T_c for a wide variety of Nb-Ge films. The width of the correlation is due in part to the large error (~25%) in

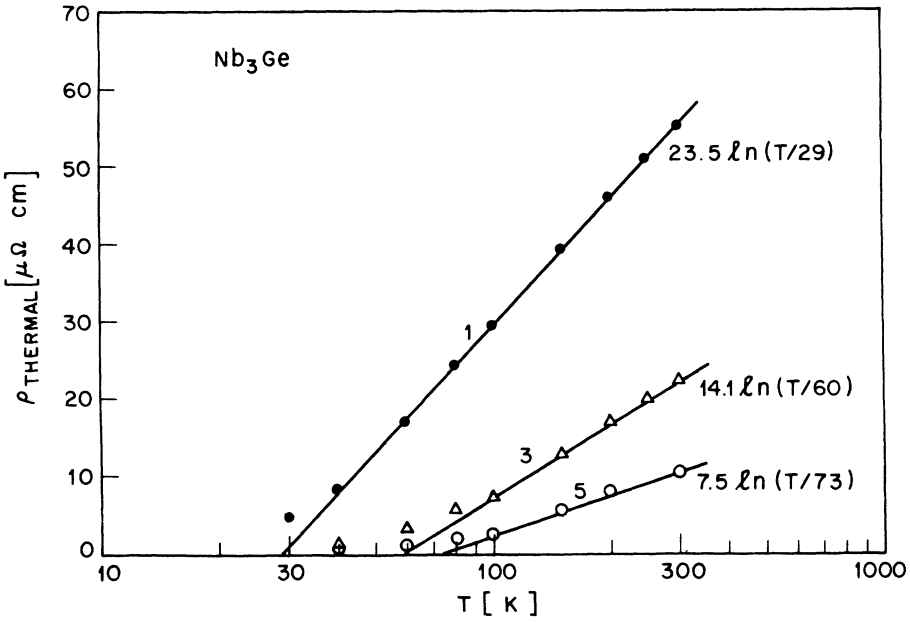

FIG. 12. Thermal part of the electrical resistivity vs ln$T$ for Nb_3Ge.

determining absolute resistivities but no doubt also reflects the fact that the relation is not exact with such wide variations in sample conditions. Note that not only can ρ_{th} achieve unusually large values (60-80 $\mu\Omega$ cm at 300 K) but that it can be varied over a very wide range, and reduced to unusually low values by the introduction of defects and by other methods which, we are assuming, also result in natural defect formation. By way of comparison, the representative point for Nb is shown. It is seen that when ρ_{th} for Nb-Ge becomes comparable to that for Nb, the T_c's are roughly comparable in magnitude. However, the same dose of ^{4}He particles (or a comparable variation in sample preparation) which varies ρ_{th} and T_c of Nb-Ge over the full range of the plot will produce in Nb changes in these quantities of an amount approximately covered by the size of the symbol used. It seems likely that Fig. 14 is a plot of T_c versus—in the Hopfield sense—the electron-phonon interaction $\lambda_{transport}$. For superconductivity, this correlation is microscopically a more meaningful one. The data clearly show the decisive role which defects can play in that interaction.

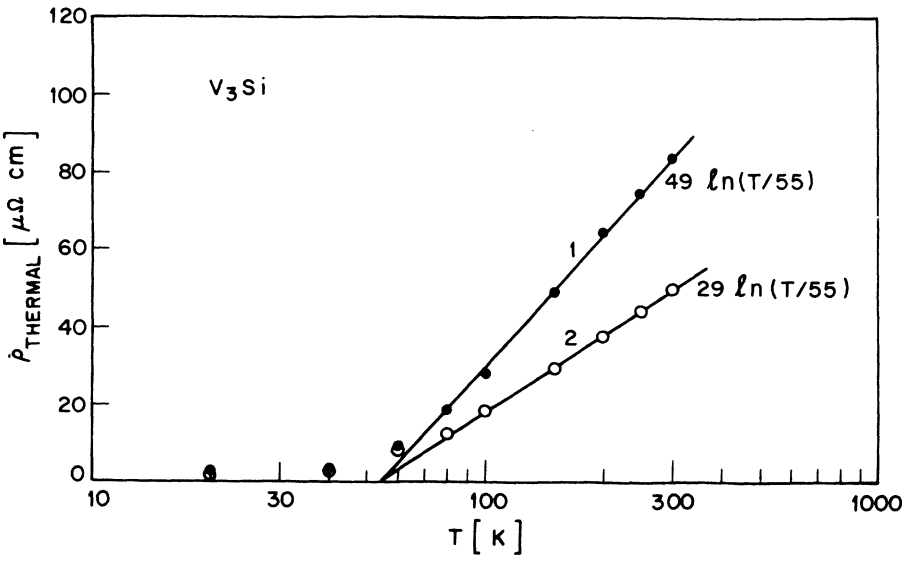

FIG. 13. Thermal part of the electrical resistivity vs ln$T$ for V_3Si.

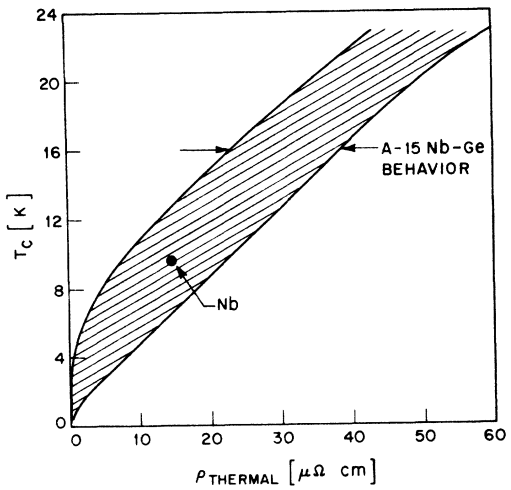

FIG. 14. T_c vs thermal part of the electrical resistivity at 300 K for Nb-Ge films.

IV. FINAL REMARKS

The possible role of defects in A-15 materials has been noted by many workers.[21] And, in retrospect, it appears that the defects may have been, in part, responsible for making the achievements of high-T_c Nb_3Ge difficult.[22] It was noted that the peculiar sputtering conditions necessary to achieve high-T_c samples were those which minimized the number of high-energy particles in the sputtering environment.[23] The damage produced in each growing layer under such conditions could lead to detrimental conditions similar in effect to that produced by the ^{4}He bombardment. While the defects may not be identical in the two cases, the similarities of the correlations of T_c with electrical resistivity and other properties (e.g., lattice parameter, critical current) suggest some similarity in the source.

The great susceptibility of the A-15 structure to damage reflects, and is no doubt the consequence of, the structural instability inherent in them. The magnitude, of course, is a matter of degree progressing from V_3Si, the least sensitive to ^{4}He damage,[13] for example, and the easiest compound to prepare, to Nb_3Ge which shows the greatest propensity to damage and where proper growth is strongly inhibited by the defects. For Nb_3Si, where the A-15 structure is more difficult to achieve, greater defect densities are required to stabilize the structure. The method to minimize the defects while retaining a reasonably ordered A-15 phase has not yet been found.

With regard to the normal-state behavior we have shown some experimental evidence of a common behavior in these materials. And it is seen that while composition alone cannot account for all of this, one can reproduce much of what is observed by the intentional introduction of defects. Thus the defects can strongly influence the normal state as well as the superconducting properties.

The exact nature of the defects is still not proven. Evidence has been published on the existence of simple antisite defects[2] and vacancies[24] but they, alone, may not be consistent with all the physical behavior published. Although such defects may surely occur, we believe—from experiments published and in progress—that what is crucial to the defect state is the existence of a disordered structure, stable at and below 300 K, and obtained by numerous small bond-bending distortions from the A-15 lattice rather than the existence of a few bond-breaking defects.

We have previously called this "the loss of the translational symmetry of the lattice—a tendency to amorphous structure with bond distortions occurring over unit cell dimensions."[25] In view of the low-site symmetry of the transition metal atoms in the A-15 structure it seems likely that the atomic displacements will not be isotropic but will, at least on a unit-cell scale, exhibit some preferred direction. Phillips[26] has recently suggested the possibility of long-range order as well. Short-range and long-range order in the defect microstate have, so far, escaped detection. Although the causes of the distortions—antisite defects, vacancies, etc.—may not be the same in every case, we suggest it is the resulting distortions which produce much of the physically significant effects and the universal behavior we have described above. Their presence is the consequence and the compromise of the structural instability.

ACKNOWLEDGMENTS

The author wishes to thank W. Royer for excellent technical assistance, J. Wernick for technical discussions, and L. Gor'kov for communicating some of his ideas to us.

[1] L. R. Testardi, R. L. Meek, J. M. Poate, W. A. Royer, A. R. Storm, and J. H. Wernick, Phys. Rev. B 11, 4304 (1975).

[2] A. R. Sweedler, D. G. Schweitzer, and G. W. Webb, Phys. Rev. Lett. 33, 168 (1974); A. R. Sweedler and D. E. Cox, Phys. Rev. B 12, 147 (1975).

[3] P. S. Swertz, H. R. Hart, and R. L. Fleischer, Appl. Phys. Lett. 4, 71 (1964); I. P. McEvoy, Jr., R. F.

Decell, and R. L. Novak, *ibid.* 4, 43 (1964); R. Bett, Cryogenics 14, 361 (1964); H. Bauer, E. J. Sauer, and D. G. Schweitzer, J. Low Temp. Phys. 19, 171 (1975).

[4]J. M. Poate, L. R. Testardi, A. R. Storm, and W. M. Augustyniak, Phys. Rev. Lett. 35, 19 (1975).

[5]D. W. Woodard and G. D. Cody, RCA Rev. 25, 392 (1964).

[6]J. E. Kunzler, J. P. Maita, E. J. Ryder, H. J. Levinstein, and F. S. L. Hsu, Bull. Am. Phys. Soc. 10, 319 (1965).

[7]M. P. Sarachik, G. E. Smith, and J. H. Wernick, Can. J. Phys. 41, 1542 (1963).

[8]M. Milewits, S. J. Williamson, and H. Taub, Phys. Rev. B (to be published).

[9]Z. Fisk and A. C. Lawson, Solid State Commun. 13, 277 (1973).

[10]L. R. Testardi, in *Physical Acoustics,* edited by W. P. Mason and R. N. Thurston (Academic, New York 1973); Vol. X, p. 193; M. Weger and I. B. Goldberg, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York 1973), Vol. 28, p. 1.

[11]H. C. Theurer and J. J. Hauser, Trans. Metall. Soc. AIME 233, 588 (1965).

[12]The resistance-ratio correlation applies to the A-15 phase in all degrees of perfection. For a Nb/Ge ratio between ~2.5 and 2, a Nb_5Ge_3 ($D8m$ structure) is also seen, and for a Nb/Ge ratio $\lesssim 2$ the samples are predominantly Nb_5Ge_3. This phase is comparatively more stable than the A-15 phase and at resistance ratios ~2 to 3 has comparably lower T_c's.

[13]J. M. Poate, R. C. Dynes, L. R. Testardi, and R. H. Hammond (unpublished).

[14]H. Lutz, H. Weismann, O. F. Kammerer, and Myron Strongin [Phys. Rev. Lett. 36, 1576 (1976)] have recently measured ρ between 4 and 575 K for a series of coevaporated Nb-Ge films with T_c's between 21 and 15 K. At least where experimental conditions overlap with ours the data appear similar. Z. Fisk and G. W. Webb [Phys. Rev. Lett. 36, 1084 (1976)] have very recently suggested that the saturation of $\rho(T)$ at high T occurs because the electron mean free path is comparable to the interatomic spacing.

[15]R. W. Cohen, G. D. Cody, and J. J. Halloran, Phys. Rev. Lett. 19, 840 (1967); see also, W. Dieterich and W. Klose, Solid State Commun. 7, 411 (1969); and R. W. Cohen and G. D. Cody, *ibid.* 7, 1379 (1969).

[16]L. R. Testardi and T. B. Bateman, Phys. Rev. 154, 402 (1967).

[17]H. Taub and S. J. Williamson, Solid State Commun. 15, 181 (1974).

[18]L. R. Testardi, Phys. Rev. B 5, 4342 (1972).

[19]P. B. Allen, J. C. K. Hui, W. E. Pickett, C. M. Varma, and Z. Fisk, Solid State Commun., (to be published).

[20]L. P. Gor'kov, Sov. Phys.-JETP 38, 830 (1974).

[21]For a historical summary and further references see R. A. Hein, in *The Science and Technology of Superconductivity,* edited by W. D. Gregory, W. N. Mathews, and E. A. Edelsack (Plenum, New York 1973), Vol. I, p. 333.

[22]J. R. Gavaler, Appl. Phys. Lett. 23, 480 (1973).

[23]L. R. Testardi, J. H. Wernick, and W. A. Royer, Solid State Commun. 15, 1 (1974).

[24]C. M. Varma, J. C. Phillips, and S.-Tsui, Phys. Rev. Lett. 33, 1223 (1974).

[25]L. R. Testardi, Solid State Commun. 17, 871 (1975).

[26]J. C. Phillips (unpublished).