Exponential temperature dependence of the electrical resistivity of V_3Si

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We report the results and interpretation of precision measurements of the electrical resistivity of V_3Si in the temperature range $T_c \leq T \leq 77$ K. Four samples of a wide range in residual resistance ratio (RRR) and with $15.1 \leq T_c \leq 16.8$ K have been investigated. We find that the resistivity of all the samples is well described by a temperature dependence of the form $\rho(T) = \rho_0 + bT^n + d\exp(-T_0/T)$, where n falls within the range $1 \leq n \leq 2$. The parameter d is sensitive to the RRR of the sample, whereas b and T_0 are relatively insensitive. The characteristic temperature $T_0 \approx 175$ K is essentially independent of the choice of n within the stated range. A similar exponential term in $\rho(T)$ of Nb_3Sn with $T_0 \approx 85$ K has previously been identified by Woodard and Cody. Noting that in *both* V_3Si and Nb_3Sn the value of T_0 corresponds to the energy of [100] TA phonons near the zone boundary, we argue that the exponential term is due either to phonon-assisted interband scattering or intraband umklapp scattering. The reasons for the scattering effectiveness of this phonon will be discussed in light of recent band-structure calculations by Mattheiss and previous band models proposed to explain the anomalous normal-state properties of A-15 compounds. The nonexponential term in the resistivity is more difficult to characterize empirically and its origin is correspondingly more uncertain. We suggest it arises from intraband electron-electron scattering. The temperature dependence of the resistivity will be discussed with respect to anomalies observed in the low-temperature elastic constants, magnetic susceptibility, and specific heat of V_3Si.

I. INTRODUCTION

Compounds with the $A-15$ crystal structure which exhibit superconductivity at relatively high temperatures (e.g., V_3Si, $T_c = 17$ K; NB_3Sn, $T_c = 18$ K; Nb_3Ge, $T_c = 23$ K) have attracted considerable interest because they also exhibit anomalous normal-state behavior. Some of these materials have a strong temperature dependence of the magnetic susceptibility, Knight shift, and elastic constants, with development of soft phonon modes and a lattice instability on cooling to low temperature (for reviews, see Refs. 1–4). We report precision measurements of the electrical resistivity in single crystals of V_3Si between T_c and 77 K which were undertaken in a search for anomalous behavior associated with phonon mode softening or fine structure in the electronic density of states. V_3Si was chosen for study, because crystals of relatively high quality (as indicated by the residual resistance ratio, RRR) were available, and the samples exhibit the anomalous normal-state behavior which is common to the $A-15$ high-T_c superconductors. Our measurements were confined to the low-temperature region where phonon mode softening and the temperature dependence of the magnetic susceptibility are most pronounced[5-7] and where effects of anharmonicity are minimal.[8]

We were initially motivated to make this study by a suggestion from Testardi and Bateman[9] that the anomaly in the resistivity of V_3Si near the cubic-to-tetrogonal martensitic transformation at a temperature T_m arises from the dramatic softening of the [110] phonon modes above T_m. Taub and Williamson[10] subsequently demonstrated through measurements on a transforming sample of V_3Si and a lower-quality nontransforming sample, with less-pronounced softening of the [110] phonon modes, that the temperature dependence of the electrical resistivities are nearly the same above T_m for the two samples. Therefore, the effect of phonon mode softening on the relevant electron-phonon scattering rates is negligible for these samples. Instead it was suggested that the resistivity anomaly at T_m is due to marked changes in the electronic density of states near the Fermi level as the lattice transforms. Such changes are evidenced by anomalies in the magnetic susceptibility for V_3Si,[7] and for Nb_3Sn ($T_m \approx 45$ K).[11]

The present measurements were undertaken to determine why phonon mode softening has little effect on the resistivity in V_3Si. Previous studies of the resistivity in[12-14] V_3Si have not focused on the mechanism of electron-phonon scattering. To our knowledge, the only other detailed studies of the resistivity in $A-15$ compounds were carried out on Nb_3Sn. One was reported by Woodard and Cody[15](WC) who developed an empirical formula to describe their data in the range $18 \leq T \leq 850$ K for several polycrystalline samples of Nb_3Sn prepared by vapor deposition. The expression

$$\rho(T) = \rho + bT + d\,e^{-T_0/T} \quad (1)$$

with a value of $T_0 = 85$ K gave a fit to better than 1% over the entire temperature range. WC suggested that the exponential term might arise from phonon-assisted interband scattering as originally proposed by Wilson.[16] He considered a two-band model with spherical Fermi surfaces in which a phonon is annihilated when it scatters an electron from a low-mass s band to a high-mass d band having a large density of states at the Fermi level. Since the Fermi surfaces are assumed to have a minimal separation q_0 in reciprocal space, the theory predicts an exponential term in $\rho(T)$ at low temperatures from the Boltzmann factor for the number of phonons with wave vector q_0 available for interband scattering. However, WC found that if the linear term in Eq. (1) is interpreted as the high-temperature limit for this interband process, the ratio d/b does not agree with Wilson's theory.[16] Therefore, they concluded that for Nb_3Sn Eq. (1) could not be interpreted consistently in terms of phonon-assisted interband scattering.

More recently a different expression has been introduced by Cohen, Cody, and Halloran[11] to describe the WC data. Their formulation is based on electron-phonon scattering in which *all* phonons can participate,[17] and they argue that the unusual temperature dependence of $\rho(T)$ is due to structure in the energy dependence of the electronic density of states. The density of states $N(E)$ in their model is assumed to be independent of E except for a discontinuity at $E = 0$. Thus they took $N(E) = \alpha N_0$ for $E < 0$ where $\alpha \ll 1$ to describe an s-electron band and $N(E) = N_0$ for $E > 0$, to describe s and d-electron bands. In this model $E = 0$ represents the bottom of the d band, and a parameter T_F is introduced to represent the Fermi energy at $T = 0$. The resistivity has a contribution from s-d scattering due to phonons and an impurity scattering term which is also temperature dependent,

$$\rho(T) = \rho_{ph}(T) + \rho_{imp}(T), \quad (2)$$

where

$$\rho_{ph}(T) \sim \left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \left(\frac{\frac{1}{2}x}{\sinh\frac{1}{2}x}\right)^2 \times \ln\left(\frac{1 + F_\alpha(T)(e^x - 1)}{1 - F_\alpha(T)(1 - e^{-x})}\right) dx,$$

$$\rho_{imp}(T) = \rho_{imp}(0)\, F_\alpha(T).$$

Here $F_\alpha(T) = [1 + e^{-E_F(T)/k_B T}]^{-1}$, and Θ is the Debye temperature. A graph of Eq. (2) is shown in Fig. 1 of Ref. 11. Values of the parameters $T_F = 100$ K and $\Theta = 250$ K are reported to give good agreement with the data. Note that at low temperatures, $T \ll T_F$ and $T \ll \Theta$, $F_\alpha(T) \sim 1$ so that Eq. (2) reduces to $\rho(T) \sim T^3$. Thus at present there are two expressions, Eqs. (1) and (2), which are reported to fit the data for the resistivity of Nb_3Sn.

For V_3Si, another low-temperature characterization has been proposed by Marchenko.[14] His data for a number of polycrystalline samples of differing quality could be approximated by

$$\rho = \rho_0 + bT^2 \quad (3)$$

to within 1% for the limited range $T_c \leq T \leq 29$ K. He interpreted the quadratic term as describing the effect of electron-electron scattering processes in which an s electron scatters with a d electron of large effective mass, leaving the two electrons in new states s' and d'.[18] A large contribution to the resistivity is expected if one band has a large density of states $N(E)$ so that the scattering rate is high. In support of this interpretation in terms of an s-d model, Marchenko noted that the ratio b/γ^2, where γ is the coefficient of the linear term of the specific heat, is approximately the same as for other transition metals where s-d scattering is believed important as pointed out by Rice.[19]

As we shall demonstrate in the following sections, the temperature dependence of the resistivity of both transforming and nontransforming V_3Si cannot be adequately described by either Eq. (2) or Eq. (3) over the temperature range $T \lesssim 77$ K. Instead, we have found good agreement with our data using a generalization of Eq. (1).

$$\rho(T) = \rho_n + b_n T^n + d_n e^{-T_0/T} \quad (4)$$

with $n = 1$, $\frac{3}{2}$, and 2. Following a description of our measurement technique in Sec. II, the empirical basis for a fit of the form Eq. (4) will be presented in Secs. III and IV. An essential aspect of this analysis is the evidence for the exponential term and the independence of the parameter T_0 on the choice of n. Section IV also treats the qualitative dependence of the parameters b_n, d_n, and T_0 on sample RRR, features which are again independent of n.

Scattering mechanisms which can yield a resistivity of the form Eq. (4) are considered in Sec. V. We attribute the exponential term either to phonon-assisted interband scattering or intraband umklapp scattering and tentatively identify the participating phonons as the [100] transverse acoustic modes near the zone boundary. Since this phonon branch does not renormalize dramatically upon cooling, the insensitivity of the resistivity to elastic softening[10] is thus explained. We note that the [100] TA phonons near the zone boundary can also account for the exponential term observed in the resistivity of Nb_3Sn.[15] The effectiveness of these phonons in electron scattering will be discussed in light of recent band-structure calculations by Mattheiss[20] and band models[11,21-23] proposed to explain the

anomalous normal-state properties of A-15 compounds.

The origin of the nonexponential term in the resistivity is more uncertain owing partly to the lack of a unique parameterization. Nevertheless, our analysis does provide the following new results concerning this term: (a) Since the nonexponential term is present at the lowest temperatures, $T \ll T_0$, it does not represent the high-temperature limit of interband scattering as considered by WC.[15] (b) The term $b_n T^n$ cannot provide a satisfactory fit if $n \geq 3$. Hence the observed resistivity is inconsistent with the low-temperature limiting behavior of Eq. (2) proposed by Cohen, Cody, and Halloran.[11] (c) The nonexponential term must be responsible for the resistivity anomaly in transforming samples since the exponential term is negligibly small near T_m. We will suggest that the nonexponential term arises from intraband electron-electron scattering which begins to dominate at low temperatures as electron-phonon scattering is frozen out.

A preliminary account of this work containing some of the measurements and a brief interpretation has appeared previously.[24]

II. EXPERIMENTAL PROCEDURES

dc electrical resistance measurements were carried out on four different single crystals of V_3Si. The samples were representative of a wide range of quality, as indicated by their residual resistance ratios $R(295\text{ K})/R(17.5\text{ K})$. We identify each sample by a number which indicates the approximate RRR, viz, VS5, VS8, VS14, and VS39.[25] Sample VS39 exhibits a martensitic transformation at about $T_m = 20.2$ K. Copper current and voltage leads were attached to each sample with indium by using an ultrasonic soldering iron. The samples have a typical size of $1 \times 1 \times 5$ mm.[3] The current was along a [100] direction. A dc current of about 40 mA was passed through the sample, causing negligible self-heating, and the voltage was detected by a Keithley 148 nanovoltmeter followed by a digital voltmeter.

The typical noise level was 3 nV, and the sample resistance could therefore be measured with a precision of ±0.02%. Periodic checks on a standard resistor permitted us to achieve an accuracy of ±0.03%. However, uncertainties in temperature calibration and control were considerably more important. We believe that our precision in resistance measurements for a given sample is better than ±0.15% in all cases. This uncertainty represents the limit to which we can compare the measured resistance with an empirical formula, such as Eq. (4).

The resistivity of VS14 was determined at room temperature by measuring the voltage between two needle-shaped probes. The distance between probes and the dimensions of the sample were measured on a Nikon viewing projector, and the results yield the geometrical factor relating resistance and resistivity. The resistivity of VS5 and VS39 had been measured by Neuringer using similar probe techniques. The uncertainty in the geometrical factor for these sample is a relatively large value of ±4% owing to irregularities in the sample shapes, and this limits the accuracy with which we can quote resistivity values. Table I summarizes data which characterize each sample. The geometrical factor for VS8 could not be determined with reliability because this sample has a highly irregular shape. We used a plot of $R(295\text{ K})$ vs RRR for the other three samples and interpolated to obtain the room-temperature resistivity. Values in Tables I and II which ultimately depend on this interpolation procedure have an estimated uncertainty of ±6% and are enclosed in parentheses. The values of T_c in Table I denote where the resistance is $\frac{1}{2}$ of the normal-state value. For VS8, VS14, and VS39 the resistive transition is about 0.2-K wide (between 10% and 90% of the normal-state resistance) and is without structure. For VS5 the width is 0.7 K, and dR/dT has a discontinuity near T_c.

III. EMPIRICAL CHARACTERIZATION

In Fig. 1 we illustrate the measured temperature dependence of the resistivity of VS14 and VS39 for the range $T_c \leq T \leq 77$ K. A resistivity anomaly at $T_m = 20.2$ K for VS39 is too weak to be seen on this scale but is illustrated in Fig. 2 of Ref. 10. To put our results in perspective, we include in an inset the resistivity of a polycrystalline sample reported by Marchenko for the range $T_c \leq T \leq 1200$ K.[14] Below 77 K where we have concentrated our study, $\rho(T)$ has positive curvature, but above ~85 K the curvature becomes negative.

For the temperature region just above T_c our data for the nontransforming samples can be fit by a quadratic dependence of the form Eq. (3) used by Marchenko.[14] Agreement to within ±0.15% can be obtained for this formula, but only up to $T \approx 26$ K. A satisfactory fit cannot be obtained over a wider temperature range. Table I lists the respective values of ρ_0 and b where it can be seen that there is no simple correlation between b and RRR. Our previous studies[10] have shown that the resistance of V_3Si above ~25 K increases more rapidly than the quadratic dependence reported by Marchenko for lower temperatures. A T^3 term can be fit to within 6% over a limited temperature

TABLE I. Superconducting critical temperature T_c; measured resistivity ρ at $T=77$ and 295 K; and empirical parameters showing the low-temperature resistivity according to the expression $\rho(T)=\rho_0+bT^2$ for $T_c<T\leq 26$ K, except for VS39 where the low-temperature limit is $T_m=20.2$ K. All resistivity values have an accuracy of 4% except for those in parentheses, whose accuracy is 6%.

Sample	T_c (K)	ρ (295 K) ($\mu\Omega$ cm)	ρ (77 K) ($\mu\Omega$ cm)	ρ_0 ($\mu\Omega$ cm)	b (10^{-3} $\mu\Omega$ cm K^{-2})
VS5	15.1	77.2	29.7	16.01	1.65
VS8	16.1	(76.0)	(23.5)	(9.00)	(1.52)
VS14	16.8	74.1	19.0	4.79	1.60
VS39	16.8	69.8	15.6	1.41	1.49

range ($25\leq T\leq 40$ K) but the data deviated systematically from such a dependence at lower and higher temperatures.[10] We therefore sought other parameterizations of $\rho(T)$.

Owing to the high T_c of these samples, it was impossible to obtain data to sufficiently low temperature that the residual resistivity could be determined reliably. Therefore, to fit empirical formulas containing more than two parameters to $\rho(T)$ or to compare the temperature-dependent portion of the resistivity of different samples, we could not follow the standard procedure of subtracting the observed residual resistivity. Instead, we have calculated the derivative $d\rho/dT$ for the four samples in the temperature range for which data at sufficiently close temperature intervals were available, and the results are shown in Fig. 2. The values of $d\rho/dT$ were calculated by fitting a parabola to five adjacent data points.[26] The results are essentially the same if a nine-point span is used instead.

Figure 2 shows that the temperature dependence of $d\rho/dT$ for all the samples is qualitatively similar, except for an anomaly near $T_m=20.2$ K for VS39. In Ref. 24 we pointed out that the inflection in the $d\rho/dT$ curves at $T\approx 38$ K indicates that the resistivity cannot be described by a power series in T with positive coefficients over the full temperature range up to 50 K. This inflection is the low-temperature precursor of the quasisaturation behavior of $\rho(T)$ at high temperatures illustrated in the inset of Fig. 1. A function that can describe the rapid increase of $\rho(T)$ above 25 K, exhibits an inflection in $d\rho/dT$ as observed, and saturates at high temperature is the exponential $d\,e^{-T_0/T}$ used in the fit to $\rho(T)$ of Nb_3Sn.[15] This motivated us to take Eq. (4) as an empirical description, and we first chose $n=2$ in order to retain a quadratic behavior at low T.

We determined the empirical parameters in Eq. (4) for $n=2$ by first plotting ρ vs T^2 which gave initial values of ρ_2 and b_2. We then used a computer to plot $\ln(\rho-\rho_2-b_2T^2)$ vs T^{-1} and adjusted ρ_2 and b_2 until a straight line was obtained for the range from T_c (or T_m) to the highest possible temperature. For each sample a straight line could be obtained at high temperature for more than two decades of variation in the value of the exponential term, as illustrated in Fig. 3. The quality of straight-line fits is very sensitive to the chosen values of ρ_2 and b_2, and consequently we could establish the "best-fit" values of these parameters with a precision of 0.2%. The accuracy of these parameters is only ±4% owing to the uncertainty in the geometrical factor used to convert resistance values to resistivities. From the plots in Fig. 3 we obtained the values of T_0 from the slope and d_2 from the intercept. Values of T_0 could be determined with an accuracy of ±2%, and d_2 with an accuracy of about ±7%. These parameters are

TABLE II. Empirical parameters characterizing the resistivity according to the expression $\rho(T)=\rho_n+b_nT^n+d_ne^{-T_0/T}$ for $T_c<T\leq 50$ K except for VS39 where the low-temperature limit is $T_m=20.2$ K. The accuracy of ρ_n and b_n is 4% while the accuracy of d_n and T_0 is 7 and 2%, respectively. Values in parentheses are subject to an additional 2% uncertainty.

	ρ_n ($\mu\Omega$ cm)			b_n (10^{-3} $\mu\Omega$ cm K^{-n})			d_n ($\mu\Omega$ cm)			T_0 (K)		
Sample	$n=1$	$n=\frac{3}{2}$	$n=2$	$n=1$	$n=\frac{3}{2}$	$n=2$	$n=1$	$n=\frac{3}{2}$	$n=2$	$n=1$	$n=\frac{3}{2}$	$n=2$
VS5	15.5	15.9	16.1	57.2	9.07	1.51	72.0	65.6	41.9	163	173	174
VS8	(8.47)	(8.91)	(9.12)	(58.0)	(8.13)	(1.31)	(87.2)	(72.2)	(47.0)	172	171	165
VS14	4.28	4.67	4.87	57.4	8.82	1.43	87.0	86.4	63.4	170	181	183
VS39	0.854	1.26	1.50	57.2	8.37	1.30	96.8	83.2	60.2	180	184	182

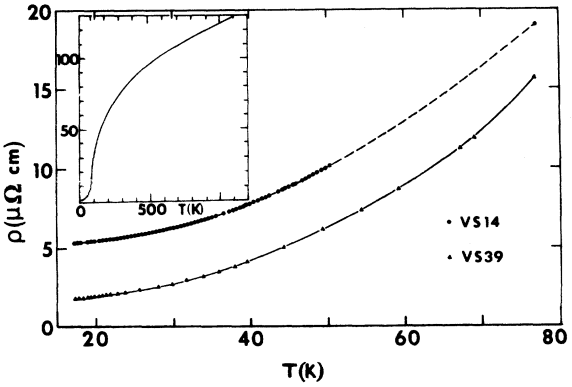

FIG. 1. Observed $\rho(T)$ for a nontransforming sample (VS14) and a transforming sample (VS39) for $T_c \leq T \leq 77$ K. Solid and dashed curves are guides to the eye. Inset with the same units on the ordinate shows $\rho(T)$ over a wider temperature range as reported by Marchenko in Ref. 14.

listed in Table II for each sample.

To illustrate the quality of the empirical description, the relative deviation between Eq. (4) and the data normalized to the *total* resistivity are summarized in Fig. 4 for each sample. It should be kept in mind that the deviation relative to the *temperature-dependent portion* of the resistivity will be correspondingly greater for samples with larger residual resistances, where the temperature-dependent portion is a smaller fraction of the total resistivity. The agreement in Fig. 4 is better than the experimental uncertainty for $T \geq 23$ K. However, a systematic deviation for all samples appears at low temperature, where the observed $\rho(T)$ falls below the values given by Eq. (4). This can be seen in the data for nontransforming VS14

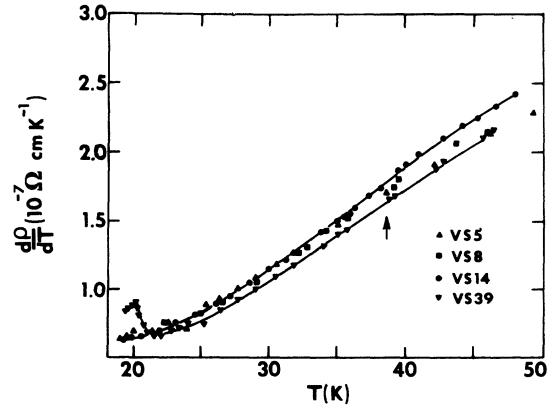

FIG. 2. Calculated values of $d\rho/dT$ based on data for four samples. Curves drawn through the data for VS14 and VS39 are guides to the eye. Inflection point in $d\rho/dT$ for VS14 is indicated by the arrow.

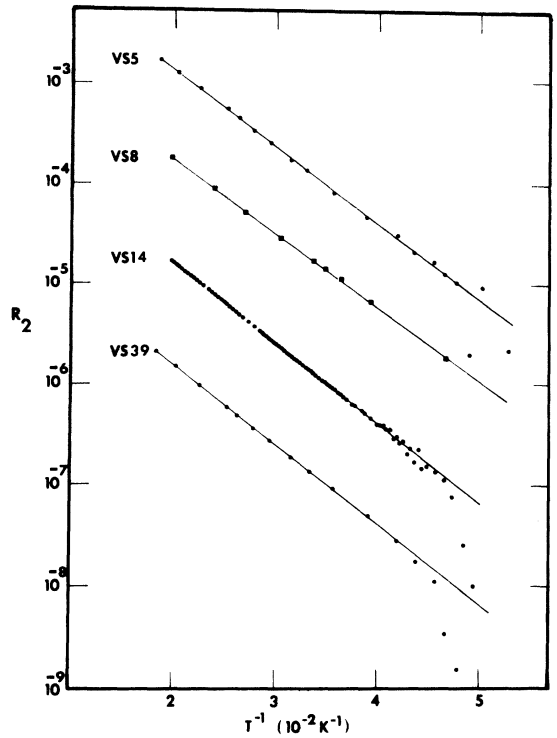

FIG. 3. $\ln R_2$ vs T^{-1}, where $R_2 = \rho(T) - \rho_2 - b_2 T^2$. Vertical axis is expressed in arbitrary units, with the data for each sample displaced vertically for clarity.

below 19 K where the discrepancy falls outside the ±0.15% uncertainty of the data and also from Fig. 3 where deviation from our exponential dependence is evident. It is not possible to improve the low-temperature fit by replacing the quadratic term with another of a form such as T^3 or T^5 as might be expected in other materials at low temperatures.

The reason for the systematic deviation at low temperature in the fit to Eq. (4) with $n = 2$ whereas none was observed in the fits to Eq. (3) is that we are demanding the T^2 term to be present over a much larger temperature range ($T \leq 50$ K). Note that the values of b_2 obtained from fits to Eq. (3) are about 10% larger than those from Eq. (4). The larger value of b_2 could be retained to fit the low-temperature data with Eq. (4) (the exponential term is negligibly small for $T \leq 23$ K), but this would lead to even larger deviations from the fit at higher temperatures.

In an effort to determine whether a term $b_n T^n$ could be used in Eq. (4) to fit the entire temperature range $T \leq 50$ K, we next considered the case $n = 1$ which had been successful in fitting Nb_3Sn.[15] The parameters ρ_1 and b_1 were adjusted to provide the best straight line for a plot of $\ln[\rho(T) - \rho_1 - b_1 T]$ vs T^{-1}. The resulting fits are illustrated in Fig. 5.

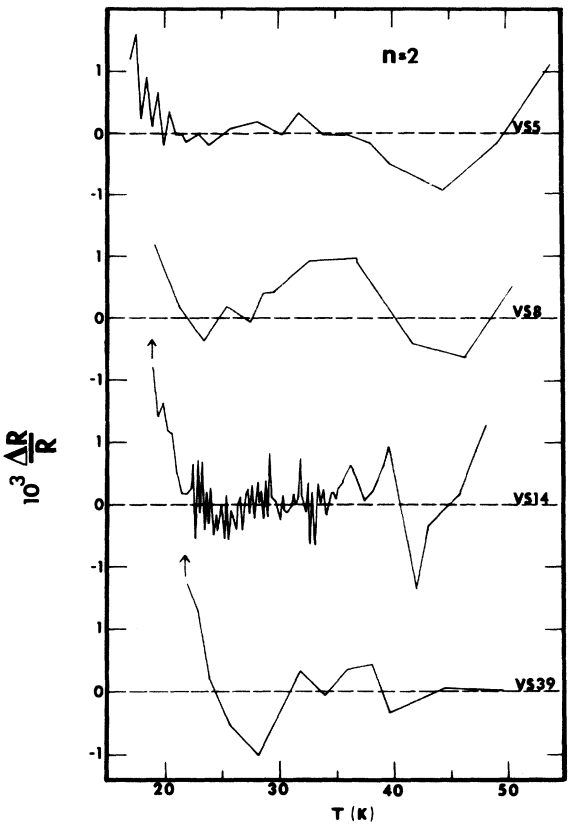

FIG. 4. Relative deviation of empirical fit compared with the observed resistivity $\rho(T)$, showing $\Delta R/R$ vs T where $\Delta R = \rho_2 + b_2 T^2 + d_2 e^{-T_0/T} - \rho(T)$. Arrows indicate where the deviation increases markedly in value.

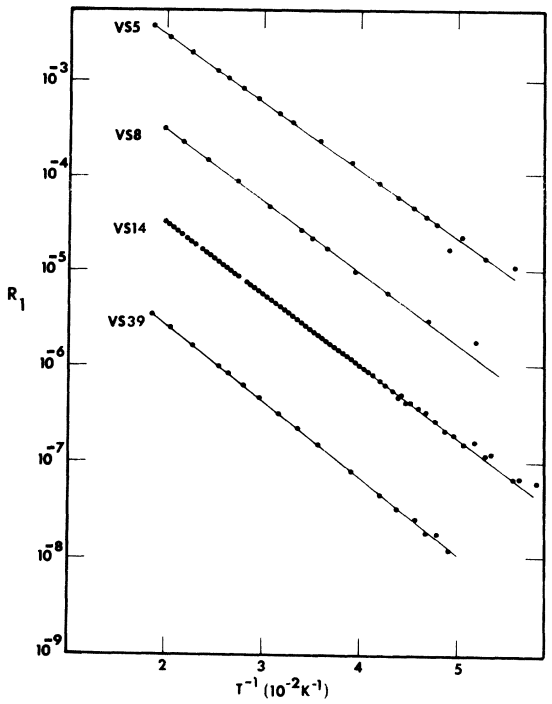

FIG. 5. $\ln R_1$ vs T^{-1}, where $R_1 = \rho(T) - \rho_1 - b_1 T$. Vertical axis is expressed in arbitrary units with the data for each sample displaced vertically for clarity.

A marked improvement was obtained at low temperatures with an exponential dependence evident all the way down to T_c in nontransforming samples. However, the quality of the fit generally worsened at higher temperatures ($T \geq 45$ K). The deviation is particularly apparent for VS39 in Fig. 6.

The last case which we considered was with $n = \frac{3}{2}$ in Eq. (4) for which a somewhat better fit to the data over the full temperature range is achieved. The plots of $\ln[\rho(T) - \rho_{3/2} - b_{3/2}T^{3/2}]$ vs T^{-1} show linear behavior down to T_c (or T_m) but the percent deviation plots display small systematic discrepancies at low and high temperatures.

The best-fit parameters ρ_n, b_n, d_n, and T_0 are listed in Table II for $n = 1$, $\frac{3}{2}$, and 2. Our empirical analysis of the resistivity based on Eq. (4) can be summarized as follows. At low temperatures ($T \leq 50$ K), an exponential term alone [$n = 0$ in Eq. (4)] cannot describe the temperature dependence of the resistivity. A choice of $n = 1$ in the term $b_n T^n$ provides a better fit at low temperatures $T \leq 45$ K, while $n = 2$ gives a better fit at high temperatures $T \geq 23$ K. Values of $n > 2$ yield a worse fit than those in the range $1 \leq n \leq 2$. If we demand that a single value of n provides the best agreement over the widest temperature range, then n must be chosen close to $\frac{3}{2}$.

IV. COMMENTS ON THE EMPIRICAL CHARACTERIZATION

It is important to note in Table II that the characteristic temperature $T_0 \approx 175$ K is relatively independent of the value selected for n. To see the reason for this, recall that the motivation for including an exponential term was to reproduce the inflection observed in $d\rho/dT$. In the fit for Eq. (4) the temperature T_i at which the inflection occurs ($d^3\rho/dT^3|_{T=T_i} = 0$) is essentially determined by T_0 and depends only very weakly on n. In fact, for *both* $n = 1$ and $n = 2$, differentiation of Eq. (4) implies $T_0 = 4.73 T_i$. Determination of T_i therefore allows an evaluation of T_0 independently of whether $n = 1$ or $n = 2$. If $n = \frac{3}{2}$, this relation is still valid to within 2% for values of $b_{3/2}$ and $d_{3/2}$ in Table II. Moreover, from our fits to Eq. (4) we would predict an inflection in ρ, i.e., $d^2\rho/dT^2 = 0$ in the range 74 to 85 K which is consistent with measurements to higher temperatures.[12,14] These considerations permit us to have some confidence in the presence of an exponential term and the value of T_0 even without a unique parameterization of the nonexponential term.

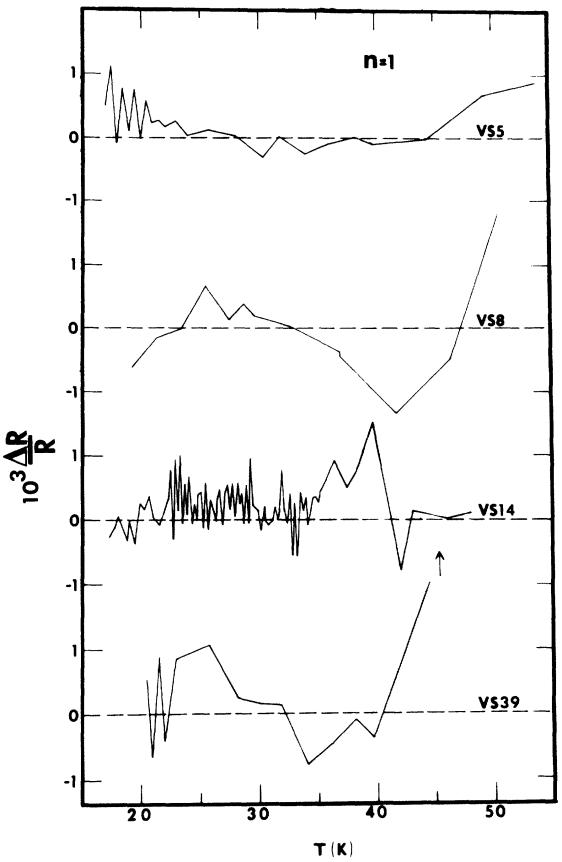

FIG. 6. Relative deviation of empirical fit compared with the observed resistivity $\rho(T)$, showing $\Delta R/R$ vs T, where $\Delta R = \rho_1 + b_1 T + d_1 e^{-T_0/T} - \rho(T)$. Arrows indicate where the deviations increase markedly in value.

On the other hand, the coefficients b_n and d_n and hence the relative magnitudes of exponential and nonexponential terms are sensitive to the choice of n. In Fig. 7 we show the relative contributions of the residual plus linear term for a choice $n=1$ (solid line) and the residual plus quadratic term for a choice $n=2$ (dashed curve) compared with the data for VS14.

The successful application of Eq. (1) to Nb_3Sn by Woodard and Cody[15] for the full span $T_c \leq T \leq 850$ K motivated us to fit it with data from V_3Si over a wider range than is covered by our measurements. We have analyzed Marchenko's data[14] for a sample with a RRR of 26 (see inset to Fig. 1) using a nonlinear least-squares fit to Eq. (1) over the temperature range $40 \leq T \leq 1200$ K. We find that agreement to better than 2% is achieved above 300 K. Below 100 K there is a ~10% discrepancy, much of which could be due to errors in reading data from Fig. 1, Ref. 14. The best-fit parameters are: $b = 36.6 \times 10^{-3}$ $\mu\Omega\,\mathrm{cm\,K^{-1}}$, $d = 104$ $\mu\Omega\,\mathrm{cm}$, and $T_0 = 161$ K which are close to the low-temperature

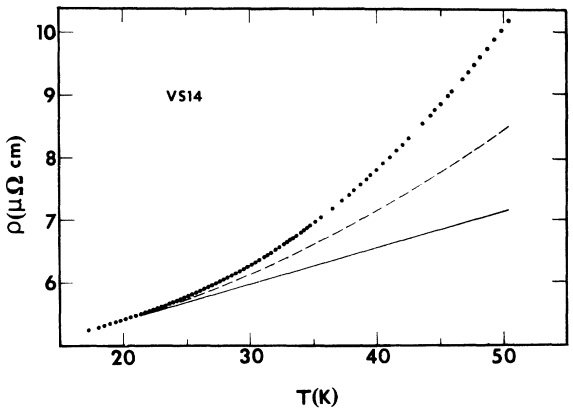

FIG. 7. Resistance of VS14 vs T (circles) compared with the resistance corresponding to the nonexponential portion of empirical fits $\rho_2 + b_2 T^2$ for $n=2$ (dashed curve) and $\rho_1 + b_1 T$ for $n=1$ (solid line).

values for $n=1$ in Table II for a sample of comparable RRR. Similar agreement cannot be obtained between low-temperature and high-temperature fits for $n=\frac{3}{2}$ and $n=2$ in Eq. (4).

It is worth noting that when $\rho(T)$ of V_3Si and Nb_3Sn are fit to Eq. (1), the coefficients b and d are quantitatively similar. The values determined by WC for a Nb_3Sn sample with RRR of 7 are $b = 46.6 \times 10^{-3}$ $\mu\Omega\,\mathrm{cm\,K^{-1}}$ which are only 20% lower than for V_3Si and $d = 74.7$ $\mu\Omega\,\mathrm{cm}$ which is virtually the same as for a V_3Si sample of comparable RRR.

An examination of the empirical parameters which are summarized in Table II reveals several systematic variations with RRR. These variations motivate us to consider first the origin of these differences in RRR. All of the crystals were grown from nominally pure starting materials, and consequently we assume that the differences arise from variations in stoichiometry. Studies by Junod *et al.*[27] for the $V_{1-X}Si_X$ system have shown that the $A-15$ phase can exist for Si concentrations in the range $0.20 \leq X \leq 0.26$. V-deficient samples were found to have nearly the same T_c as those with the correct stoichiometry ($X=0.25$); but V-rich samples have values of T_c that decrease markedly with decreasing X. Thus we believe that VS5 and VS8 are V rich as indicated by their low values of T_c, whereas VS14 and VS39 are nearly stoichiometrically correct, as indicated by their high values of RRR and high T_c. In addition, we note that studies by Kunzler *et al.*[28] for nearly stoichiometric samples show that T_c increases with increasing RRR up to a value of $T_c \approx 17.2$ K, corresponding to RRR ≈ 20, and then decreases with further increase in RRR. Samples with RRR ≥ 20 generally transform at least partially to the tetragonal phase above T_c, and so their lower T_c

may characterize the tetragonal and not the cubic phase. From this trend we deduce that although our VS14 and VS39 samples have the same T_c, they would be characterized by positions on opposite sides of the maximum in a plot of T_c vs RRR.

The resistivity analysis which we summarize in Tables I and II indicates that normal-state transport properties as well as T_c depend upon RRR. Whether we choose $n=1$, $\frac{3}{2}$, or 2 for the empirical characterization in Eq. (4) the resulting values of T_0 and d_n are found to increase with RRR. The variation of T_0 amounts to ~10%, whereas the change in d_n is ~30%. It is remarkable that d_n has such a strong dependence on RRR, especially when compared with the much weaker variation of other physical properties such as T_c, Debye temperature, and coefficient of the linear term of the specific heat γ.[27] The coefficient b_n is essentially the same for all samples for a given n, with variations on the order of the uncertainty. This sample-independent feature is particularly apparent for the case $n=1$.

V. INTERPRETATION

A. Exponential term

The outstanding feature of our results is the identification of an exponential term in the resistivity of V_3Si similar to one reported by Woodard and Cody for Nb_3Sn. Such a term is characteristic of a thermally activated scattering mechanism. Although we cannot unambiguously identify its origin, we shall offer some plausible arguments for this term originating in phonon-assisted interband or intraband umklapp scattering. In the former case, first considered by Wilson,[16] the characteristic temperature T_0 appearing in the exponential term corresponds to the energy of a phonon with minimum wave vector required to scatter an electron between bands. For intraband electron-phonon umklapp scattering T_0 corresponds to the energy of a phonon with wave vector matching a particular dimension of a single sheet of the Fermi surface.[29]

Neutron scattering studies on V_3Si by Shirane, Axe, and Birgeneau[30] indicate that a number of phonons have the energy $\hbar\omega/k_B = T_0 \approx 175$ K, and therefore a unique identification of the relevant modes cannot be made on the basis of this energy alone. However, if we assume that the modes responsible for the exponential term have the same symmetry in both V_3Si and Nb_3Sn, a plausible assignment can be made. For most directions in the Brillouin zone, phonon energies in Nb_3Sn are 60 to 80% of the corresponding modes in V_3Si. Only for the transverse acoustic branches along the [100] directions is this percentage as low as 50%, which is approximately the ratio of $T_0 = 85$ K for Nb_3Sn and $T_0 = 175$ K for V_3Si. Indeed, at room temperature the [100] TA modes at the Brillouin-zone boundary have energies of $\hbar\omega/k_B = 88$ and 184 K for Nb_3Sn[31] and V_3Si, respectively, which are very close to the observed values of T_0. Thus we tentatively identify these modes as giving rise to the exponential term in $\rho(T)$. The appropriate wave vector for phonon-assisted scattering is then $q_0 \approx \pi/a$, where a is the lattice constant.

Tunneling measurements indicate that electron-phonon coupling is appreciable for the [100] TA phonons near the Brillouin-zone boundary. Shen[32] has observed a pronounced maximum in the weighted phonon density of states $\alpha^2F(\omega)$ for Nb_3Sn at an energy of 8 meV (94 K) slightly higher than $T_0 = 85$ K as measured by Woodard and Cody. There is also some evidence in tunneling measurements by Hauser on V_3Si for a peak in $\alpha^2F(\omega)$ at 14.3 meV (167 K)[1], which is close to our value of T_0 for samples of low RRR. The case for identifying these peaks in $\alpha^2F(\omega)$ as coming from TA phonon modes near the Brillouin-zone boundary in the [100] direction has been stated in some detail by Testardi.[1] The identification is based on the form of the phonon density of states $F(\omega)$ which has been estimated for V_3Si and Nb_3Sn by Testardi and Mattheiss[1] using data obtained from neutron scattering and ultrasonic studies. For V_3Si a sharp peak at 15.5 meV is calculated for $T = 300$ K which shifts to 14.5 meV for $T = 17$ K. The peak is associated with the energy of the [100] TA branch at the zone boundary, although a large portion of $F(\omega)$ is also contributed by zone-boundary TA phonon modes in the [110] direction. For Nb_3Sn a marked peak is found at about 9 meV for $T = 300$ K, with a shift to about 7 meV on reducing temperature to $T = 46$ K. Again, the peak is associated with the TA phonon modes in the [100] direction at the Brillouin-zone boundary.

It might be argued that the phonons responsible for the exponential term in $\rho(T)$ are selected by a sharp peak in the phonon density of states $F(\omega)$ at $\omega_0 = k_B T_0/\hbar$. However, we have calculated the density of *occupied* states $F(\omega)n(\omega)$ where $n(\omega) = [\exp(\hbar\omega/k_B T) - 1]^{-1}$ is the phonon occupation number, using the estimated $F(\omega)$ of Testardi and Mattheiss[1] for V_3Si. For $T \leq 50$ K, $F(\omega)n(\omega)$ is a monotonically decreasing function of ω showing no fine structure at ω_0. Therefore, we believe the selection of particular phonons must come from a topological constraint of the Fermi surface as in Wilson's theory.

Very little is known concerning the Fermi surfaces of $A-15$ compounds. Only in V_3Ge have experiments revealed definite features of the Fermi surface.[33] The most detailed description

of the band structure is provided by a recent augmented-plane-wave linear-combination-of-atomic-orbitals (APW-LCAO) band-structure calculation by Mattheiss.[20] His results indicate that the Fermi surface may be quite complicated. Bands near E_F are predominantly of d character associated with V atoms. A narrow band lies close to E_F near Γ at the zone center and crosses E_F at several places within the zone. Broader bands cross near the zone corners R and midpoints of the zone edges M. At R and M several band extrema lie near E_F, so pockets of small dimensions could be located there. Although the accuracy of Mattheiss's results are believed to be substantially improved over previous calculations, a shift of certain bands by only 10 mRy relative to E_F produces major alterations in the Fermi surface. In view of the uncertainties in the parameters of this calculation we choose to use the APW-LCAO result primarily as a guide as to where carrier pockets are likely to be found.

There are several features of the band structure calculated by Mattheiss which can be related to the scattering effectiveness of [100] TA phonons of wave vector $q_0 \approx \pi/a$. One possibility is that these phonons assist interband scattering between carrier pockets located at the R and M points of the cubic Brillouin zone. The pockets would have to be small and at least one must have a high density of states at the Fermi level. The first condition is required for the phonon wave vector $q_0 \approx \pi/a$ to span the distance between pockets. The latter condition ensures that the interband scattering occurs with high probability, dominating other scattering mechanisms. Small hole pockets at the R point with a high density of states have been recently proposed by Gor'kov[23] to explain the anomalous properties of V_3Si and Nb_3Sn. In his coupled linear-chain model, the martensitic transformation is viewed as lifting the degeneracy of the bands at R thereby reducing the electronic free energy. This Jahn-Teller effect can qualitatively explain the temperature dependence of the soft elastic constants and the magnetic susceptibility.

One of the more reliable features of Mattheiss's calculation is a relatively-high-mass electron band at the Brillouin-zone center. Mattheiss claims the cyclotron mass of this band to be 2–3 times larger than for hole orbits near the R and M points and suggests that it provides the main contribution to the density of states $N(E_F)$. In this case, we believe the most effective electron-phonon scattering would be umklapp processes in which the relatively large electron wave vector is reversed by scattering to the opposite side of the band.[34] For [100] TA phonons near the zone boundary to umklapp scatter preferentially would require fairly flat regions of the Fermi surface normal to the [100] directions and separated by a distance π/a. These conditions are fulfilled reasonably well in Mattheiss's calculation for V_3Si. The location of the Fermi level is such that the electron band is very nearly calipered by a wave vector of magnitude π/a along a [100] direction. This is not true of Nb_3Sn, however, where the predicted Fermi level lies too high in the electron band. Unfortunately, the narrowness of the band and the uncertainty in E_F prevent the Fermi-surface dimensions along [100] from being determined reliably.

It is interesting to note that conduction along the [100] directions is an essential feature of the early band models of the $A-15$ compounds. Weger[21] first suggested that the unusual properties of these materials is due to the transition-metal atoms forming three orthogonal linear chains in the [100] directions. Labbé and Friedel[22] later used this idea by treating one-dimensional d bands associated with each chain in the tight-binding approximation. In these simplified models one would expect strong coupling of the d electrons to phonons propagating along the chain direction. The Fermi surface consists of intersecting planes normal to the [100], but the caliper in these directions $2k_F \ll \pi/a$ is much smaller than for the heavy electron band in Mattheiss's calculation. Other differences between the APW-LCAO band-structure and the one-dimensional models have been discussed in detail by Mattheiss.[20]

The selection of phonons of a particular *wave vector* to explain the exponential term in the resistivity of V_3Si and Nb_3Sn is unrelated to the model proposed by Cohen *et al.*[11] The characteristic temperature which enters their expression for the resistivity [Eq. (2)] corresponds to the Fermi energy rather than a phonon energy. They are able to fit the strong temperature dependence of the resisitivity of Nb_3Sn above T_m by having the Fermi level pass through a step-discontinuity in the density of states.

In Sec. IV we discussed the dependence of the parameters T_0 and d_n in the exponential term on sample RRR. We conclude the present discussion with some remarks on how this dependence can be related to a model of phonon-assisted interband scattering. The listing in Table II shows a small ~10% increase in T_0 for a given n as RRR increases from 5 to 39. This could arise from a variation of the wave vector q_0 of the strongly coupling phonon owing to changes in the Fermi-surface dimensions. It could also result from a variation in phonon energy for a given q_0, since there is evidence from specific-heat measurements for a decrease in Debye temperature with an excess V concentration.[27]

The more dramatic ~30% increase in d_n with RRR for a given n suggests an increase in the scattering rate owing to changes in the electron density of states $N(E_F)$. An increase in $N(E_F)$ could be expected from improvement in crystalline order or a change in d-electron concentration as ideal stoichiometry is approached. This interpretation is qualitatively consistent with band models[11,22,23] where $N(E_F)$ is sensitive to both crystalline order [35,36] and the carrier concentration. If the dependence of d_n on RRR is associated with a change in $N(E_F)$, we might expect a similar dependence on γ, the coefficient of the linear term in the specific heat. Junod *et al.*[27] observed γ to increase with RRR, although the effect is not as large as we have found for d_n. A quantitative comparison is not possible due to problems of extracting γ from the specific-heat measurements. Also, in some of the band models[11,22], the d electrons may be nondegenerate in which case γ is not proportional to $N(E_F)$.

B. Nonexponential term

We turn now to consider the cause of the remaining temperature-dependent term in $\rho(T)$. It should be recognized that a separation of the resistivity into terms b_nT^n and $d_ne^{-T_0/T}$ may be complicated by a small temperature dependence of the parameters b_n, d_n, and T_0. For example, the neutron scattering experiments[30] show the phonon energy corresponding to T_0 in Nb_3Sn decreasing 12% from room temperature to T_m. In our analysis of the resistivity, such departures from pure exponential behavior have been included in the term b_nT^n. This may be the reason for obtaining reasonably good fits to the resistivity with both $n=1$ and 2 depending on which portion of the temperature range is emphasized. Thus, it is difficult to identify the origin of the nonexponential term by a well-defined power-law behavior; rather, we discuss those results which are independent of a particular value of n in the range $1\leq n\leq 2$.

In analyzing $\rho(T)$ of Nb_3Sn for evidence of phonon-assisted interband scattering, WC[15] assumed this scattering mechanism to be present alone with a rate proportional to the occupation number of a particular phonon n_{q_0}. The terms bT and $d\,e^{-T_0/T}$ in Eq. (1) were identified with the asymptotic behavior of n_{q_0} in the high- and low-temperature limits, respectively. In this case one expects $b/d\approx 1/T_0$ which is about an order of magnitude larger than they found for Nb_3Sn. It was on this basis that they rejected Wilson's model for interband scattering. Although we find a similar discrepancy between b_1/d_1 and T_0^{-1} for V_3Si (see Table II), our low-temperature measurements conflict with this interpretation. The nonexponential term in the resistivity is present at temperatures $T\ll T_0$ so that it cannot represent the high-temperature limiting behavior of n_{q_0}. Consequently, we do not find the WC argument for rejecting the Wilson theory compelling.

The expression Eq. (2) which Cohen *et al.*[11] subsequently used to fit the resistivity contains both impurity and electron-phonon interband scattering terms. At low temperatures the temperature dependence of ρ is dominated by the electron-phonon term which has a T^3 rather than an exponential dependence. This is because there is no selection on the wave vector of the participating phonons.[17] However, our analysis in Sec. III shows that a term b_nT^n with $n\geq 3$ does not provide a satisfactory fit to the low-temperature resistivity of V_3Si. The failure of both an exponential and T^3 temperature dependence in V_3Si below 50 K suggests that there may be another scattering mechanism present at low temperatures in addition to the electron-phonon interaction.

There are a number of other scattering mechanisms which may be important and give rise to a term of the form b_nT^n, $1\leq n\leq 2$, in the resistivity. Marchenko[14] has argued for a T^2 term due to *intraband* electron-electron scattering[18] because the ratio b/γ^2 is close to the values obtained for other transition metals.[19] We believe this conclusion should be treated with caution since the temperature range over which the T^2 dependence occurs is so limited. A further complication in identifying the origin of the nonexponential term is that band models[11,22,23] suggest that the d electrons may be nondegenerate. As shown in several model calculations for nondegenerate bands, a $T^{3/2}$ term in the resistivity can result from either interband electron-electron scattering[37] or intraband electron-phonon scattering.[17] The point which we have labored to make in Sec. III is that our fits to Eq. (4) are not sufficiently conclusive to distinguish between a $T^{3/2}$ and a T^2 term at low temperatures.

The most persuasive evidence we find to support Marchenko's contention of a large electron-electron scattering contribution to the resistivity comes from samples which exhibit a martensitic transformation. Whatever the origin of the term b_nT^n, it must be responsible for the resistivity anomaly near T_m in these samples. In our fits to Eq. (4) for the transforming sample VS39, the exponential term $d_ne^{-T_0/T}$ is less than $\frac{1}{2}$% of the total resistivity at $T_m=20.2$ K. The decrease in $\rho(T)$ below T_m caused by the transformation is larger than this and therefore cannot be attributed to a suppression of the exponential term. At 17.5 K the observed ρ is $\gtrsim$2.4% below the value predicted by Eq. (4). This could be accounted for by a re-

duction of the coefficient b_n of $\gtrsim 5\%$ between T_m and 17.5 K. Such a decrease in b_n could be explained by electron-electron scattering within a degenerate band. In this case, the coefficient of the T^2 term varies as $N^2(E_F)$.[19] Assuming $N(E_F)$ proportional to the magnetic susceptibility $\chi(T)$, the observed decrease in $\chi(T)$ below[7] T_m is large enough to account for the change in b_2. However, the type of Fermi-surface distortion necessary to explain the temperature dependence of $\chi(T)$ must await a more detailed calculation of the band structure.

VI. CONCLUSIONS

We have found that the strong temperature dependence of $\rho(T)$ in V_3Si can be described by an exponential term similar to that observed in Nb_3Sn. The coefficient of the exponential term depends strongly on stoichiometry or crystalline order as measured by the sample RRR. We attribute this term to phonon-assisted interband or umklapp scattering. Using neutron scattering data, we have tentatively identified the relevant phonons in *both* V_3Si and Nb_3Sn as belonging to the [100] TA branch with wave vector $q_0 \approx \pi/a$. In our interpretation these phonons are selected by a characteristic dimension of the Fermi surface: either the distance in reciprocal space separating two carrier pockets or a caliper of a single sheet of the Fermi surface. However, a more detailed model of the Fermi surface is needed to confirm this proposal.

There is a more weakly temperature-dependent term which dominates the resistivity at low temperatures to which we attribute the resistivity anomaly in transforming samples. This term may be due to electron-electron scattering within a band having a large and temperature-dependent density of states.

We have found no evidence for pronounced effects in the resistivity from phonon mode softening. In our view, this is because the exponential term does not involve phonons which soften appreciably while the nonexponential term is likely due to electron-electron scattering.

The evidence we find in the normal-state resistivity for strong electron-phonon coupling at a particular wave vector, $q_0 \approx \pi/a$, could have important implications for understanding the high-temperature superconductivity of the $A-15$ compounds. If a strong q dependence of the electron-phonon interaction is responsible for the exponential term in the resistivity, one might expect a similarly strong q dependence of the electron-phonon coupling parameter α. Indeed, this is an inherent feature of the early one-dimensional theory of superconductivity[38] in which phonons of wave vector $q = 2k_F$ couple strongly to the conduction electrons. It is not, however, customarily taken into account in recent calculations of T_c based on the McMillan formula.[39] The present results suggest that the q dependence of α in $A-15$ superconductors should be examined.

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