# Far-infrared measurements of Holstein processes and low-energy $\alpha_{tr}^2F(\omega)$ structure in $V_3Si$

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Far-infrared measurements in thin films of $V_3Si$ at 19 K give evidence of Holstein processes. An analysis according to Allen's formulation yields a transport electron-phonon spectral function $\alpha_{tr}^2F(\omega)$ which is enhanced at low energies relative to the phonon spectrum alone and exhibits a new peak at $6(\pm 2)$ meV. The enhancement and structure strongly influence calculated values of $T_c$ and the electron-phonon parameter $\bar{\lambda}_{tr}$ for $V_3Si$. The Holstein analysis resolves a large discrepancy between far-infrared and near-infrared values for the plasma frequency.

## I. INTRODUCTION

Information about the electron-phonon coupling is difficult to determine in metals and metallic superconductors. Far-infrared measurements can yield data about the electron-phonon spectral function $\alpha^2F(\omega)$. Such analyses have been made in lead[1–4] but have had very limited application in the $A$-15 materials. In the only previous work, the far-infrared reflectivity of bulk $V_3Si$ was qualitatively examined to suggest the positions of peaks in $\alpha^2F(\omega)$ but the analysis did not give the full shape or magnitude of the spectral function.[5] In this paper we present the first complete quantitative analysis for an $A$-15 superconductor, made with transmission data from thin films of $V_3Si$. We extract frequency-dependent scattering times and plasma frequencies from our data, and attribute these dependences to Holstein processes. An analysis according to the theory of Allen[6] then yields the coupling parameter for transport processes, $\alpha_{tr}^2F(\omega)$, as well. These results show an enhancement in $\alpha_{tr}^2F(\omega)$ at low frequencies as compared with the phonon density of states $F(\omega)$, and a new peak at $6(\pm 2)$ meV. Both may play a significant role in the normal- and superconducting-state properties of $V_3Si$, as we show with calculations based on our derived $\alpha_{tr}^2F(\omega)$.

## II. EXPERIMENTAL PROCEDURES AND RESULTS

We examined two films of $V_3Si$ grown by dc getter sputtering on sapphire (0001) substrates.[7] Both samples were of unusually high quality for their small thicknesses with the characteristics shown in Table I. The thicknesses were found to within 15% by Rutherford backscattering and independently from the known growth rates. The $\omega \rightarrow 0$ far-ir behavior depends on the dc sheet conductance $\sigma_0 d$ (where $\sigma_0$ is the dc film conductivity and $d$ is the film thickness) which we measured directly to within 3%. Visual examination showed both films to be uniform and free of pinholes.

Data were taken between 0.6 and 35 meV with three different Fourier spectrometers. The 20-nm film was examined at Emory University at 300 K. Details of the reflection and transmission results, and of the Emory spectrometer have been given elsewhere.[8] The same spectrometer was used to measure the reflection of the 78-nm film at 19 and 300 K, but the transmission was too small to measure. Two spectrometers, also described elsewhere,[9] were used at The Ohio State University to determine the transmission of the 20-nm film at 19 K and these results are shown in Fig. 1. The displayed quantity is $T_{rel}$, the transmission of the film-substrate system divided by the transmission of the substrate alone, which is convenient for calculation.

## III. ANALYSIS

Since the skin depth ($\delta$) of the far-ir radiation in these films is much greater than the mean free path, the electrodynamics can be analyzed using a local theory. In particular, for metallic films with $\delta$ greater

 

TABLE I. dc characteristics of the $V_3Si$ samples; film thickness $d$, residual resistivity ratio (RRR) $\rho(300\ K)/\rho(19\ K)$, sheet resistance at 19 K $R_\square$, resistive superconducting transition temperature $T_c$.

| Sample | $d$ (nm) | RRR | $R_\square$ (Ω) | $T_c$ (K) |
|---|---|---|---|---|
| 1 | 20 | 3.21 | 18.4 | 15.0 ±0.5 |
| 2 | 78 | 7.05 | 1.52 | 15.7 ±0.3 |

than $d$, $T_{rel}$ is given by an expression due to Tinkham[10]

$$T_{rel}=\left[\left(1+\frac{y_1}{n+1}\right)^2+\left(\frac{y_2}{n+1}\right)^2\right]^{-1}, \qquad (1)$$

where $n$ is the refractive index of the substrate and $y=y_1+iy_2=(4\pi/c)\sigma d$ is the dimensionless sheet conductance of the film. The substrate absorption is canceled out to first order in the above expression. Multiple reflection effects are negligible in the thin film at 300 K and give only a small correction at 19 K.

The low-frequency conductivity in metals can be expressed in the Drude form

$$\sigma=\sigma_0/(1+i\omega\tau), \qquad (2)$$

where $\sigma_0=\omega_p^2\tau/4\pi$, $\omega_p$ is the plasma frequency, and

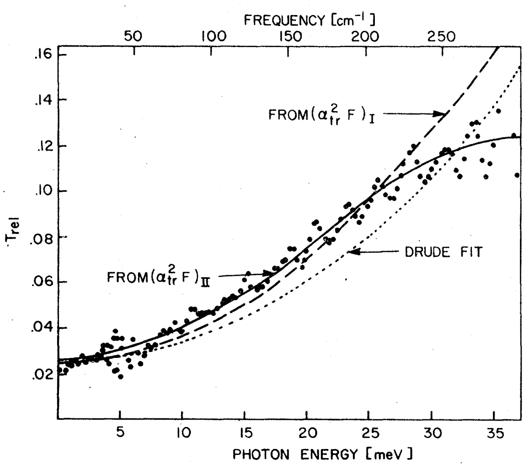


FIG. 1. Measured values of the relative transmission $T_{rel}$ vs energy and theoretical fits as described in the text. The oscillations in the data above 15 meV arise from interference fringes in the optically flat sapphire substrates which are incompletely cancelled out in the ratio. The apparent structure centered near 5 meV is due to the overlap between the two Fourier spectrometers and has no physical significance. The Drude fit is made with the fixed values $\omega_p=1.8$ eV and $\tau=5\times10^{-14}$ sec.

$\tau$ is the scattering time. For the 20-nm film at 300 K where $\omega\tau \ll 1$ (dirty limit) $T_{rel}$ is essentially constant and was accurately predicted by Eqs. (1) and (2) using the dc value of $\sigma_0 d$.[8] Even where a strong frequency dependence was seen, at low temperature and in the thicker film, the $\omega\to0$ transmissions and reflectivities were given to within ~4% by the dc film sheet conductances. This agreement is slightly worse than is usually achieved for films in the dirty limit, possibly because of the difficulty in determing the exact $\omega=0$ intercept of frequency-dependent reflections and transmissions. Since the measured $T_{rel}$ follows the dc temperature dependence, giving good agreement with the dc sheet conductance at both 300 and 19 K, the evidence is strong that Drude electronic conduction processes dominate in the far-ir behavior. For the optical properties to be affected by interband transitions would require an appreciable coincidence of bands near the Fermi energy with a spacing less than $\hbar\omega$. In the low-frequency far-ir spectral region ($\hbar\omega<35$ meV) this is extremely unlikely. Also such fine structure in the density of states is barely compatible with the energy resolution of ~15 meV implied by the scattering in these films.

In the simple Drude model it is assumed that the far-ir frequency dependence is given by Eq. (2) with a constant $\omega_p$ and $\tau$. Our transmission results at low $T$ and higher $\omega$, however, are not well described by this model (see Fig. 1). Attempts to force fit the relation for the thin film $T_{rel}$ at 19 K yield $\omega_p=1.8$ eV but increasing with frequency, and $\tau=5\times10^{-14}$ sec but decreasing with frequency. Reflectivity measurements on the thicker film at 300 K, while less sensitive than transmission, gave a value of 1.2 eV for $\omega_p$. These results are very far from the value of 2.8 eV determined for thicker $V_3Si$ films at 300 K in the near-ir,[11] and from the theoretical result $\omega_p=3.2$ eV obtained from augmented plane wave (APW) calculations.[12]

Frequency-dependent plasma frequencies and relaxation times are known to result from the effect on the conductivity of the electron-phonon interaction, the Holstein process.[13] Such a process would result in an enhancement of the electronic optical mass (or $1/\omega_p^2$) for frequencies less than or near the characteristic phonon frequency of the metal, with the enhancement approaching zero at much higher frequencies. The measured plasma frequency, therefore, should increase from the far-ir to a near-ir value which closely agrees with band-structure calculations that exclude electron-phonon effects. In addition, the Holstein process will produce dissipative effects because of the spontaneous emission of phonons by the optically excited electron. This would cause a reduction in relaxation time with frequency. Both expectations qualitatively agree with our observations.

These arguments have been put on a quantitative basis by Allen,[6] who has shown that the Holstein process can be included in the Drude form [Eq. (2)] with the replacements

$$\omega_p^2 \rightarrow \omega_p^2/[1+\bar{\lambda}_{tr}(\omega)]\ , \tag{3}$$

$$\tau \rightarrow \tau^*(\omega) = \bar{\tau}(\omega)[1+\bar{\lambda}_{tr}(\omega)]\ ,$$

where the mass enhancement parameter $\bar{\lambda}_{tr}(\omega)$ and the frequency-dependent relaxation time $\bar{\tau}(\omega)$ are given in terms of the transport electron-phonon coupling factor $\alpha_{tr}^2F(\omega)$ at absolute zero by

$$\bar{\lambda}_{tr}(\omega) = 2\int_0^\infty \frac{d\omega'}{\omega'}\,\alpha_{tr}^2F(\omega')\left[\frac{\omega'}{\omega}\ln\left|\frac{\omega+\omega'}{\omega-\omega'}\right| + \left(\frac{\omega'}{\omega}\right)^2\ln\left|\frac{\omega^2}{\omega'^2}-1\right|\right]\ ,$$

$$\frac{1}{\bar{\tau}(\omega)} = 2\pi\int_0^\omega d\omega'\,\alpha_{tr}^2F(\omega')\left(1-\frac{\omega'}{\omega}\right)\ . \tag{4}$$

Only the transmission data on the 20-nm film at 19 K were sufficiently sensitive to absorptive processes and of sufficient quality to allow a comparison with this theory. To determine if the data on this film are consistent with Allen's theory, we generated a plot of $T_{rel}$ versus frequency from Eqs. (1) through (4) (Ref. 14) assuming that $\alpha_{tr}^2F(\omega)$ is proportional to the phonon spectrum $F(\omega)$. This spectrum has been found by neutron scattering measurements[15] and is shown in Fig. 2. The proportionality constant was chosen so that the McMillan[16] superconducting parameter $\lambda = \bar{\lambda}_{tr}(0) = 1$. (We assume here that the transport coupling factor $\alpha_{tr}^2$ is the same as the superconducting coupling factor $\alpha^2$.) The result of this calculation is shown in Fig. 1 by the curve marked I. As can be seen the general shape is correct and the fit is much improved over the original Drude fit with constant $\omega_p$ and $\tau$, although the fit is not yet ideal. The residual resistivity has been included in the analysis by the addition of a constant impurity scattering time $\tau_i$ such that

$$\frac{1}{\tau^*(\omega)} = \left(\frac{1}{\bar{\tau}(\omega)} + \frac{1}{\tau_i}\right)/[1+\bar{\lambda}_{tr}(\omega)]\ , \tag{5}$$

$\tau_i^{-1}$ was set equal to $0.5\times10^{14}$ sec in generating curve I.

We interpret the difference between curve I and our data as arising from additional structure in $\alpha_{tr}^2F(\omega)$. To determine this we have made a fit to the data using Eqs. (1)–(5) to obtain the best values for $\alpha_{tr}^2F(\omega)$ and $\tau_i$. The computer fit was made by numerically integrating over an $\alpha_{tr}^2F(\omega)$ which was approximated by Lorentzian oscillators. The highest-frequency oscillator, which had only a small (~5% in $\bar{\lambda}_{tr}$) effect on the fit, was fixed at 42 meV to agree with the peak in $F(\omega)$ but with reduced amplitude.[17] A second oscillator was placed in the range of the major phonon peak and its position and strength were varied to fit the data. In addition to these two oscillators which are directly related to the phonon spectrum, it was found necessary to add a third low-frequency oscillator where the only indication of structure in the phonon spectrum is that $F(\omega)$ does not approach zero as $\omega \rightarrow 0$. On its low-frequency side, this third Lorentzian was modified to approach zero as $\omega^2$.

The three-oscillator $\alpha_{tr}^2F(\omega)$ which gave the best fit to our data is displayed in Fig. 2, and the fit to $T_{rel}$ itself is shown in Fig. 1 as curve II. The latter fit is now very good. The best fit $\alpha_{tr}^2F(\omega)$ required a strong peak at 6 (±2) meV and a shift in the middle

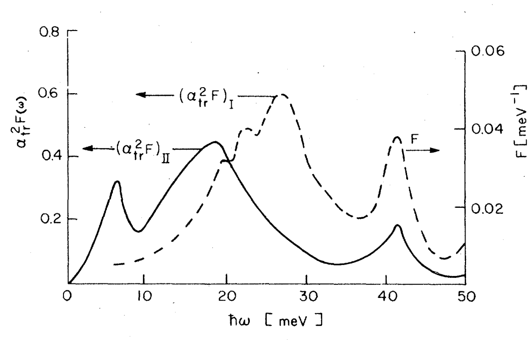


FIG. 2. Phonon spectrum $F(\omega)$ obtained from neutron scattering (Ref. 15), $\alpha_{tr}^2F(\omega)$ for constant $\alpha_{tr}^2$ and $\bar{\lambda}_{tr}=1$ (curve I), and the best fit result for $\alpha_{tr}^2F(\omega)$ (curve II).

peak from about 25 meV in the phonon spectrum down to 18 meV in $\alpha_{tr}^2F(\omega)$. Evidence for this low-energy enhancement of $\alpha_{tr}^2F(\omega)$ can be directly seen in the data (Fig. 1). The decrease in slope of $T_{rel}$ indicates that $\alpha_{tr}^2F(\omega)$ is already exhausted by 25 meV, implying that a major peak exists below this energy. This result is independent of any uncertainties in the fitted parameters. In addition to generating $\alpha_{tr}^2F(\omega)$, our fitting procedure returned the value

$$\tau_i^{-1}=0.5\times10^{14}\,\mathrm{sec}^{-1}\,.$$

The heights and widths of the peaks in $\alpha_{tr}^2F(\omega)$ are not independently determined to much accuracy in the numerical fits since $T_{rel}$ is given roughly by $\int\alpha_{tr}^2F(\omega)$. Thus, for example, a 6 (±2) meV peak with about half the amplitude and twice the width would fit the data with only somewhat reduced precision. However, many important parameters depend on $\int\alpha_{tr}^2F(\omega)$ and the corresponding uncertainties are reduced [for example, to ~15% in $\bar{\lambda}_{tr}(0)$-see below] with the fit values quoted.

The $\bar{\lambda}_{tr}(\omega)$ and $\bar{\tau}(\omega)^{-1}$ calculated from our $\alpha_{tr}^2F(\omega)$ are shown in Fig. 3. With the use of $\bar{\lambda}_{tr}(0)$ and $\tau^*(0)$ from these plots, the bare plasma frequency $\omega_p$ (excluding Fermi-liquid effects) can be extracted from both the dc conductivity and the $\omega\to0$ transmission data. Both calculations give the same result, $\omega_p=2.7\pm0.2$ eV, completely resolving the discrepancy between the far-ir and the near-ir values.

The dramatic increase in low-energy electron-phonon coupling indicated by our results may have important implications for the superconducting behavior of $V_3Si$. Table II shows the coupling parameter $\bar{\lambda}_{tr}(0)$ and weighted average phonon frequencies calculated from the $\alpha_{tr}^2F(\omega)$ we have determined. For comparison, the same quantities are shown as calculated from the room-temperature phonon spectrum $F(\omega)$, where we assumed that $\bar{\lambda}_{tr}\sim1/\langle\omega^2\rangle$. Finally the $T_c$ calculated from McMillan's formula[16] with $\mu^*=0.11$ and $\bar{\lambda}_{tr}(0)=\lambda$ is shown for both cases. This choice of $\mu^*$, which is in the middle of the range of estimated values, allows us to predict the exact $T_c$ of the film. The importance of the low-energy enhancement is clearly shown by the large increase in $\lambda$ and in $T_c$.

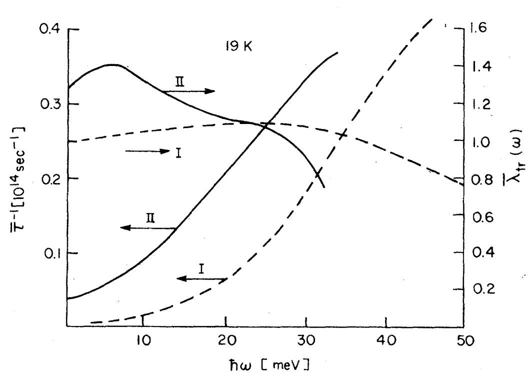


FIG. 3. $\bar{\lambda}_{tr}(\omega)$ and $\bar{\tau}(\omega)^{-1}$ as calculated from $[\alpha_{tr}^2F(\omega)]_I$ and $[\alpha_{tr}^2F(\omega)]_{II}$.

TABLE II. Summary of findings as calculated from $F(\omega)$ and from the present $\alpha_{tr}^2F(\omega)$ data. Formulas for the quantities in the Table are given in Ref. 16. $F(\omega)$ is taken from Ref. 15.

| | From present $\alpha_{tr}^2F(\omega)$ With low $\omega$ peak | From present $\alpha_{tr}^2F(\omega)$ Without low $\omega$ peak | From $F(\omega)$ (300 K) |
|---|---|---|---|
| $\langle\omega\rangle$ (meV) | 13.8 | 16.3 | ~24 |
| $\langle\omega^2\rangle^{1/2}$ (meV) | 16.7 | 19.3 | 27.6 |
| $\bar{\lambda}_{tr}(0)$ | 1.29 | 0.98 | 0.48[a] |
| $T_c$ (K) (with $\mu^*=0.11$) | 15 | 12 | 2.4 |

[a]Obtained by scaling $\lambda_{tr}\propto(1/\langle\omega^2\rangle)$ to present data.

The increase in $\alpha_{tr}^2$ below 20 meV occurs in the same energy region where $F(\omega)$ shows most of its softening with decreasing temperature.[15] Assuming that this increase is related to the phonon softening accompanying the structural instability, we can compare the predictions for $T_c$ and $\lambda$ with no $\alpha_{tr}^2$ enhancement to the behavior of (radiation damaged or nonoptimally prepared) samples that have no instability or phonon softening. In such samples the low-$T$ phonon behavior is similar to room-temperature behavior in intrinsic samples but they have a $T_c$ of 2–3 K and a $\lambda$ of about 0.45–0.55.[18] This is in agreement with the values calculated in Table I for $F(\omega)$ at 300 K.

## IV. CONCLUSIONS

We have interpreted far-ir transmission data in thin-film $V_3Si$ according to the theory of Holstein processes as given by Allen and have extracted a detailed form for $\alpha_{tr}^2F(\omega)$. This analysis has brought into agreement the far- and near-ir values for the plasma frequency. Our results clearly show the existence of low-energy structure and enhancement in $\alpha_{tr}^2F(\omega)$ beyond what is seen in the phonon spectrum alone, with suggestive consequences for the superconducting behavior. Although earlier bulk $V_3Si$ experiments[5,19] have pointed to the existence of $\alpha^2F(\omega)$ peaks at 6 ±2 and 14–15 ±2 meV, the present work puts the low-energy behavior on a firm footing for the first time.

Apart from the specific applicability of $V_3Si$ and its superconducting behavior, the far-infrared technique applied here offers a method for examining electron-phonon behavior in metals[20] to supplement techniques such as cyclotron resonance which require single crystals of high quality. Since it can also be applied at temperatures above $T_c$, it can potentially yield information on the temperature dependence of $\alpha_{tr}^2F(\omega)$ which may relate to the numerous normal state anomalies of the $A$-15 materials as well.

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