Microwave Response of $V_3Si$ Single Crystals: Evidence for Two-Gap Superconductivity

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Abstract

The investigation of the temperature dependences of microwave surface impedance and complex conductivity of $V_3Si$ single crystals with different stoichiometry allowed to observe a number of peculiarities which are in remarkable contradiction with single-gap Bardeen-Cooper-Schrieffer theory. At the same time, they can be well described by two-band model of superconductivity, thus strongly evidencing the existence of two distinct energy gaps with zero-temperature values $\Delta_1 \approx 1.8T_c$ and $\Delta_2 \approx 0.95T_c$ in $V_3Si$.

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The story of multi-gap superconductors goes to the middle of the last century, when the extension of Bardeen-Cooper-Schrieffer (BCS) theory \cite{1} was proposed \cite{2, 3}. The followed experimental investigations, however, contradicted each other showing the existence of single gap, multiple gaps and slightly anisotropic gap in various superconducting materials. The interest to this phenomenon has been stimulated by the discovery of two-gap superconductivity in MgB$_2$. The existence of at least two different energy bands crossing the Fermi-level (particular feature of MgB$_2$) appears to be the prerequisite for the observation of multiple gaps. The second requirement, as follows from \cite{3}, is a weak interband scattering. Such processes can be significantly reduced if wave functions of electrons from two bands have different symmetry. For example this may happen when energy band structure has both flat and non-flat areas near the Fermi level. Flat areas lead to a singularity in the density of states at the Fermi level and can be experimentally detected for instance by non-linear temperature dependence of the resistivity $\rho(T)$ in the normal state. In the opposite case of more or less similar bands structures even small amount of impurities leads to high interband scattering and almost excludes the possibility to detect multi-gap response of the material.

Apparently, the above requirements apply to the layered superconductorNbSe$_2$ and to A15 structure superconductors Nb$_3$Sn, V$_3$Si, V$_3$Ga, in which the density of states has very high and narrow peak just in the vicinity of the Fermi level according to band-structure calculations \cite{4}. Recently the existence of multiple gaps in Nb$_3$Sn polycrystalline sample has been proposed to explain specific heat measurements \cite{5}. The authors of \cite{6} showed the similarity of the magnetic field dependence of thermal conductivity in NbSe$_2$ to that of MgB$_2$ and concluded about the presence of the second energy gap in NbSe$_2$. Such a similarity was not found in V$_3$Si. However, back in 1969 J.Brock denoted the existence of the second gap as one of the possible explanations of the peculiarities seen in the specific heat of V$_3$Si \cite{7}.

The measurements of the temperature dependences of microwave conductivity both in low-$T_c$ and high-$T_c$ superconductors were very informative. They proved the applicability of BCS theory to conventional superconductors, allowed to distinguish superconductors with different order parameter symmetry and to measure the values of energy gap, penetration depth, quasiparticles relaxation rate, mean free path, that are the quantities important for comparison with first-principles calculations. In the $c$-axis oriented MgB$_2$ films an anomalous peak in the real part of conductivity around $T/T_c = 0.6$ was observed \cite{8}. Its origin is associated with the smallness of the gap in a dirty two gap superconductor. However, up
to now there was no successful preparation of MgB$_2$ samples series with different impurity concentration and falling into dirty and pure limit. A15 materials which preparation technology is well established seem to be the best candidates for the detailed study of two-gap superconductivity.

In this Letter we present investigation of the temperature dependences of microwave surface impedance $Z(T) = R(T) + iX(T)$ and complex conductivity $\sigma(T) = \sigma'(T) - i\sigma''(T)$ of V$_3$Si crystals with different degree of imperfection and critical temperatures. The activation energy $\Delta_2$ of low-temperature dependences $\delta X \propto \exp(-\Delta_2/T)$ amounts to $\Delta_2(0) \approx 0.95 T_c$, that is much smaller than BCS value $\Delta(0) = 1.76 T_c$. The so-called coherent peak appearing in $\sigma'(T)$ of less perfect sample is located at $T \approx T_c/2$, that is lower than BCS value $T \approx 0.85 T_c$. The curve of $\sigma'(T)$ in the clean sample has no peak at all. The dependences $\sigma''(T)$ of both samples demonstrate an evident inflection at temperature $T \approx T_c/2$. The observed peculiarities are in remarkable contradiction with single-band BCS model but can be well fitted by two-band model of superconductivity thus evidencing the existence of two distinct energy gaps with zero-temperature values $\Delta_1 \approx 1.8 T_c$ and $\Delta_2 \approx 0.95 T_c$ in V$_3$Si.

Two single crystals of V$_3$Si were investigated. Sample #1 had stoichiometric composition, that is 25% of silicon, whereas #2 was prepared with 1% of silicon deficiency. Both samples having rectangular shape were preliminary polished and cleaned to remove possible surface contamination. Measurements of the ac-susceptibility at 100 kHz showed the superconducting transition temperatures $T_c = 16.5$ K and $T_c = 12.5$ K for samples #1 and #2, respectively, and the transitions widths less than 0.2 K.

The microwave experiments were performed by the "hot-finger" technique [9, 10]. We placed the sample into the center of the cylindrical superconducting niobium cavity resonating at the frequency $f = \omega/2\pi = 9.4$ GHz in TE$_{011}$ mode and having high unloaded quality factor $Q_0 \approx 2 \times 10^7$. Since the sample is located at the antinode of the microwave magnetic field, the resonance frequency $f(T)$ of the system and its quality factor $Q(T)$ can be easily related to the surface impedance $Z(T) = R(T) + iX(T)$ of the sample using simple formulas [10]. The real part, surface resistance $R(T)$, is proportional to the microwave power absorbed by the sample, whereas the imaginary part, surface reactance $X(T)$, is the reactive component which defines the electromagnetic field screening. In the superconducting state when $R(T) \ll X(T)$ surface reactance directly gives the magnetic field penetration depth $\lambda(T) = X(T)/\omega\mu_0$, where $\mu_0 = 4\pi \times 10^{-7}$ H/m. The main three advantages of this technique
are (i) the sensitivity in the superconducting state of even small crystal being high enough to detect the change in \( \lambda(T) \) amounting to parts of a nanometer, (ii) the possibility to obtain the value of \( \lambda(0) \) and to measure (iii) the normal state conductivity.

The results of the surface impedance measurements in the temperature range \( 2 \leq T \leq 100 \text{ K} \) are shown in Fig. 1. In the normal state the data on both samples demonstrate the equality \( R(T) = X(T) \) from \( T \simeq 35 \text{ K} \) and up to 300 K thus conforming the validity of the normal skin effect. This makes possible to obtain the resistivities \( \rho(T) = 2R^2(T)/\omega\mu_0 \) shown in the inset to Fig. 1. Nonlinear temperature dependence of \( \rho(T) \) in the entire temperature range points to a singularity in the density of states in \( \text{V}_3\text{Si} \). Low value of the resistivity \( \rho(T_c) \approx 2 \mu\Omega\cdot\text{cm} \) is indicative of high purity of the sample #1. The non-stoichiometric sample #2 shows 20 times higher resistivity \( \rho(T_c) \).

A quasiparticle relaxation time \( \tau \) near the transition temperature can be estimated from the standard formula of the Gorter and Casimir two-fluid model \( \omega\tau(T_c) = X^2(0)/2R^2(T_c) \): \( \omega\tau(T_c) \approx 0.06 \) and 0.006 for samples #1 and #2, respectively. Rather large value of \( \tau \) in the sample #1 leads to the non-zero value of the imaginary part of the normal state conductivity (time dispersion of the Drude conductivity) and causes the discrepancy between \( R(T) \) and \( X(T) \) curves in Fig. 1 at \( 17 < T < 35 \text{ K} \). We get parameter \( \gamma = 1/\tau(T_c) \): \( \gamma \approx 7 \text{ K} \) for sample #1 and \( \gamma \approx 70 \text{ K} \) for sample #2. From \( T_c \) values we can estimate the amplitudes of the superconducting gaps using BCS relation \( \Delta(0) = 1.76T_c \). We have \( \Delta(0) \approx 30 \text{ K} \) for sample #1 and \( \Delta(0) \approx 20 \text{ K} \) for sample #2. Combining the above obtained values we conclude that sample #1 can be classified as clean superconductor \( (\Delta > \gamma) \), whereas sample #2 falls into the dirty limit \( (\Delta < \gamma) \).

In Fig. 2 the dependences of \( \ln[X(T) - X(0)] \) on \( T_c/T \) are shown. Since in the London superconductor \( [X(T) - X(0)] \propto \exp[-\Delta(0)/T] \), the slopes of the linear at \( T < T_c/3 \) sections of these graphs (solid lines in Fig. 2) directly give us the values \( \Delta_2(0)/T_c = 0.97 \) and \( \Delta_2(0)/T_c = 0.93 \) for samples #1 and #2, respectively. These values are approximately half in comparison with the standard BCS value.

In the superconducting state we find the values of zero-temperature penetration depth \( \lambda(0) = X(0)/\omega\mu_0 \) being equal 150 nm and 180 nm for samples #1 and #2, respectively. \( \text{V}_3\text{Si} \) can be classified as London superconductor in which the coherence length \( \xi(0) \approx 5 \text{ nm} \) at \( T = 0 \) is much less than the magnetic field penetration depth. So, the relationship between the impedance and complex conductivity is given by local formula \( \sigma = i\omega\mu_0/(R + iX)^2 \). To
obtain the temperature dependences of complex conductivity we use the values \( X = X(T) \) and \( R = R(T) - R_{\text{res}} \), where \( R(T) \) and \( X(T) \) are shown in Fig. 1 and \( R_{\text{res}} = R(T \to 0) \) is so-called residual surface resistance. Below 4 K surface resistance curves of both samples rich the plateau which enables us to determine \( R_{\text{res}} \) values amounting to 1.7 ± 0.02 mΩ and 0.24 ± 0.02 mΩ in samples #1 and #2, respectively. The account for \( R_{\text{res}} \) does not change \( \sigma''(T) \) but influences \( \sigma'(T) \).

The inflection seen in \( X(T) \) curve in Fig. 1 at \( T \approx 10 \) K for the sample #1 becomes more evident when looking at the imaginary part \( \sigma''(T) \) of the conductivity shown in Fig. 3. Moreover, quite similar inflection persists also in the second sample. No such an inflection is predicted by the single-gap BCS model (dashed and dotted lines in Fig. 3). The accuracy of our method (less than 1 nm for \( \delta\lambda(T) \)) and the fact that we directly extract the absolute value \( \lambda(0) \) of the penetration depth suggest that the peculiarities of \( \sigma''(T) \) curves can not be caused by an experimental error. For the sake of comparison in the same figure we show also our measurements of the conductivity \( \sigma''(T) \) of Pb\(_{2-x}\)Mo\(_6\)S\(_8\) crystal (Chevrel phase) which is well fitted by BCS theory.

Fig. 4 demonstrates the temperature dependences of the real part of the conductivity \( \sigma'(T) \). It is well known that in the dirty limit of BCS model there is a pronounced coherence peak in \( \sigma'(T) \) dependence. Its maximum corresponds to the condition \( \Delta(T) \approx T \) which happens at \( T \approx 0.85T_c \). The dotted line in Fig. 4 shows \( \sigma'(T) \) curve for dirty BCS superconductor with \( T_c = 12.5 \) K. However, dirty sample #2 has a broad peak centered at \( T \approx 0.5T_c \). Its position is only slightly affected by the choice of \( R_{\text{res}} \) and by no means can be shifted to the BCS value. The curve of \( \sigma'(T) \) in sample #1 has no peak because the coherence peak disappears in the clean limit of the BCS model (dashed line in Fig. 4).

The peculiarities of \( \sigma(T) \) curves in Figs. 3 and 4 can be explained in the framework of simplified two-band model with free parameters of intraband (\( g_{11} \) and \( g_{22} \)) and interband coupling (\( g_{12} \) and \( g_{21} \), chosen to be equal for simplicity). In the model \[ g_{11}, g_{22} \] the values of superconducting gaps \( \Delta_i \) in two bands can be obtained from the following set of equations:

\[
\Delta_1 = g_{11}\Delta_1 I(\Delta_1) + g_{12}\Delta_2 I(\Delta_2), \quad \Delta_2 = g_{21}\Delta_1 I(\Delta_1) + g_{22}\Delta_2 I(\Delta_2) \quad (1)
\]

\[
I(\Delta_j) = \int_0^{\frac{\omega_c}{2}} \frac{\tanh(\sqrt{z^2 + \Delta_j^2})}{\sqrt{z^2 + \Delta_j^2}} dz.
\]

Fig. 5 shows the temperature dependences of superconducting gaps calculated by Eq. (1)
for the values of coupling parameters indicated in Fig. 3. Parameter $g_{11}$ defines the critical temperature $T_c$ and larger gap $\Delta_1$, whereas $g_{22}$ affects mainly the smaller gap $\Delta_2$ and, thus, the low-temperature behavior of the surface impedance.

Using the obtained gaps values we can calculate the temperature dependences of conductivities $\sigma_j(T) = \sigma_j'(T) - i\sigma_j''(T)$ in each band ($j = 1, 2$) using the following generalization of formulas (12):

$$\frac{\sigma_j(T)}{\sigma_j'(0)} = -\frac{i}{2} \left[ \int_{\Delta_j - \omega}^{\Delta_j} \{I\} \tanh(\frac{\omega + \omega'}{2T})d\omega' + \int_{\Delta_j}^{\infty} \left( \{I\} \tanh(\frac{\omega + \omega'}{2T}) - \{II\} \tanh(\frac{\omega'}{2T}) \right) d\omega' \right]$$

$\{I\} = \frac{g + 1}{\varepsilon_- - i\gamma} + \frac{g - 1}{-\varepsilon_+ - i\gamma}$, $\{II\} = \frac{g + 1}{\varepsilon_- - i\gamma} + \frac{g - 1}{\varepsilon_+ - i\gamma}$,$\quad g = \frac{\omega'(\omega' + \omega) + \Delta_j^2}{\sqrt{\omega'^2 - \Delta_j^2} \sqrt{(\omega' + \omega)^2 - \Delta_j^2}}$,

$$\varepsilon_- = \sqrt{(\omega + \omega')^2 - \Delta_j^2} - \sqrt{(\omega')^2 - \Delta_j^2}, \quad \varepsilon_+ = \sqrt{(\omega + \omega')^2 - \Delta_j^2} + \sqrt{(\omega')^2 - \Delta_j^2}.$$

Then, neglecting the interband impurity scattering, which is expected to be much weaker than intraband scattering, we get the total microwave conductivity as a sum of conductivities (2) in two bands (13). The inflection of $\sigma''(T)$ curve is mainly affected by $g_{12}$. If $g_{12} = 0$, then we have two independent BCS gaps, each opening at its own critical temperature. The temperature dependence of $\sigma''(T)$ will contain a sharp inflection point corresponding to the opening of the smaller gap $\Delta_2$. If $g_{12} > 0$, but rather small, then both superconducting gaps will open at the same transition temperature and the inflection in $\sigma''(T)$ curve will be smoothed. The results of such calculations are shown in Fig. 3 by solid lines. One can easily see that the change of $g_{12}$ for samples #1 and #2 is in a good agreement with the evolution of experimental $\sigma''(T)$ curves for these samples, that is, the dirtier sample the greater interband coupling. Note also that gap-to-$T_c$ ratios occurred to be almost the same for both samples, namely, $\Delta_1 \approx 1.8T_c$ and $\Delta_2 \approx T_c$.

Theoretical calculations of $\sigma'(T)$ curves with the same parameters as in Fig. 3 and the fitting values of the relaxation rates in two bands are shown in Fig. 4 by solid lines. The shift of $\sigma'(T)$ maximum for sample #2 to $T \approx 0.5T_c$ is explained by the fact that the coherence peak arises from the energy band with the smaller gap $\Delta_2$ at $\Delta_2(T) \approx T$. In contrast to the excellent agreement between the calculations and experimental data on $\sigma''(T)$ in Fig. 3, only the qualitative agreement takes place for $\sigma'(T)$. The possible reason of quantitative difference may be caused by the simplification of the theoretical model used. For example, it does not account for the interband scattering and strong coupling effects.

In the absence of detailed calculations of $V_3Si$ Fermi surface we cannot treat the data in
the framework of an anisotropic $s$-wave model of superconductivity. However, the calculated temperature dependence of NMR relaxation rate (analogue of $\sigma'(T)$) for oblate $\Delta(k)$ gap anisotropy does not show significant difference from the standard BCS model. The appearance of the inflection on $\sigma''(T)$ in the model is also quite unlike.

In conclusion, the real and imaginary parts of the microwave conductivity were measured in two $V_3Si$ crystals with different silicon content, purity regime and $T_c$ values. The results obtained cannot be explained by single-band BCS model of superconductivity. At the same time they can be well described by two-band theory. In both samples the values of gap-to-$T_c$ ratios are approximately the same, namely, the large gap is $\Delta_1 \approx 1.8 T_c$ and the smaller one is $\Delta_2 \approx T_c$. This experimental evidence of two energy gaps in $V_3Si$, which seemed earlier to be conventional BCS-superconductor, can be confirmed also by our preliminary microwave measurements of $V_3Si$ crystals with silicon content lowered down to 20%.

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Figure 1: Temperature dependences of the surface resistance (squares) and reactance (circles) of sample #1 (solid symbols) and #2 (open symbols). Inset shows the resistivities in the normal state of the samples.
Figure 2: Surface reactance in the logarithmic scale versus $T_c/T$ (the data for sample #1 are shifted up by 2). The slopes of the linear at $T < T_c/3$ sections of these curves directly give the values of the smaller gap $\Delta_2(0)$. Single gap BCS slope is shown by dashed line.
Figure 3: Experimental temperature dependences of the imaginary part of the conductivity in samples #1 (circles), #2 (squares), and Pb$_{2-x}$Mo$_6$S$_8$ crystal (diamonds). Solid lines stand for the case of weak-coupling two-band theory with the parameters listed in the corner. Dashed, dotted and dash-dotted lines show single-band BCS calculations for $T_c = 16.5, 12.5,$ and $13.6$ K respectively.
Figure 4: Temperature dependences of the real part of the conductivity of samples #1 (circles) and #2 (squares). Solid lines show the calculations in the framework of two-band model with the same parameters as in Fig. 3. Relaxation times used for fitting are shown in the corner of the plot. Dashed line stands for the single-band BCS result for clean superconductor with $T_c = 16.5$ K. Dotted line corresponds to dirty BCS limit and $T_c = 12.5$ K.
Figure 5: Solid and dashed lines show the temperature dependences of superconducting gaps $\Delta_1$ and $\Delta_2$ calculated by Eq. (1) for superconductor with $T_c = 16.5$ K. Dotted and dash-dotted lines stand for the case of $T_c = 12.5$ K.