Electronic Raman Scattering by Superconducting-Gap Excitations in Nb_3Sn and V_3Si

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Raman-scattering measurements on Nb_3Sn and V_3Si show new peaks in the superconducting state close in energy to the superconducting gap 2Δ. These are attributed to direct electronic Raman scattering by pairs of superconducting quasiparticles. A theory is presented which fits the data well and provides evidence for anisotropy of the gap ($\sim 20\%$ in Nb_3Sn) and of the matrix element for electronic Raman scattering.

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Direct electronic Raman scattering by superconducting-gap excitations was first predicted over two decades ago[1]; however, its observation has been hampered by experimental difficulties. Theoretical calculations of the Raman-scattering spectrum of a superconductor[1-3] have all been made in the limit where the optical penetration depth, δ, is small compared to the superconducting coherence length, ξ_0. They predict a discontinuous turnon at the gap, 2Δ, which asymptotically approaches the linear background of the normal metal. In this Letter, we report observations of direct electronic Raman scattering by superconducting-gap excitations. New peaks appear, close in energy to 2Δ, in disagreement with existing theories, but adequately described by a theory for the limit $\delta \gg \xi_0$. These results provide evidence for anisotropy of both the gap ($\sim 20\%$ in Nb_3Sn) and the Raman-scattering matrix element (which is closely related to the inverse effective-mass tensor). Thus, detailed information on the basic microscopic interactions responsible for superconductivity can be derived from the Raman-scattering spectrum. A brief report of some aspects of this work has already appeared[4,5]; the theoretical interpretation given below now rests on a firmer foundation.

The A-15 compounds Nb_3Sn and V_3Si are noteworthy for their high-temperature superconductivity and various electronic and phonon anomalies.[6] For the O_h point group only excitations with E_g, T_{2g}, or A_{1g} symmetry can be Raman active. One E_g, one T_{2g}, and no A_{1g} optical phonons are expected in the A-15 structure. Raman studies of the E_g optical phonon show that it has a strongly temperature-dependent, asymmetric line shape—evidence of strong electron-phonon coupling.[7-10]

All data were obtained with 514-nm laser light incident at a pseudo-Brewster angle of $\sim 70°$; the 40-mW beam formed an $0.1 \times 2.5\text{-mm}^2$ illuminated area. The scattered light was collected in a direction normal to the surface. When the samples were not immersed in superfluid helium, laser heating was sufficient to drive them normal.

Figure 1 shows Raman spectra from a Nb_3Sn

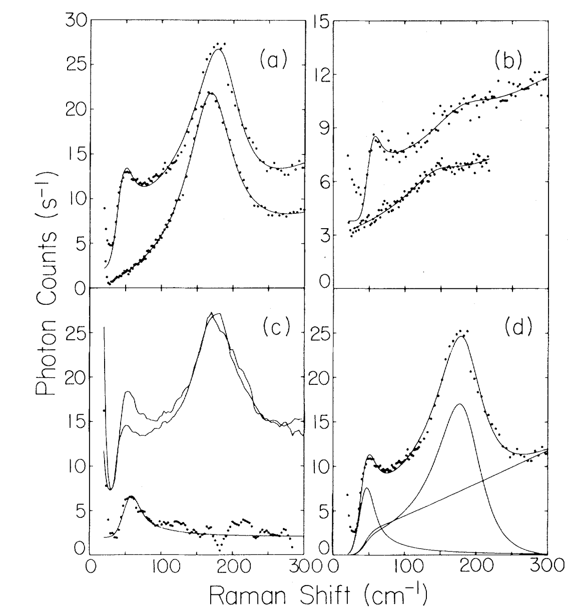

FIG. 1. Raman spectra of Nb_3Sn. Lower curves in (a) and (b) are at 40 K and upper curves are at 1.8 K. Data in (c) and (d) are at 1.8 K. Symmetries are (a), (d) E_g; (b) T_{2g}; (c) top, $E_g + A_{1g}$; middle, E_g; bottom, A_{1g}. The A_{1g} data in (c) are obtained by subtraction from the upper two curves in (c). All solid lines except the upper two in (c) are theoretical fits.

single crystal in various polarization geometries at 40 and 1.8 K. The sample was grown by closed-tube vapor transport. Other samples from the same growth were measured to have $T_c = 18.0$ K and a residual resistivity ratio (RRR) extrapolated to 0 K of 50, and underwent a martensitic transformation at $T_m = 50.6$ K. The Raman-active E_g optical phonon appears near 175 cm^{-1} in the E_g and $E_g + A_{1g}$ spectra. This mode can be thought of as a charge-density wave (CDW) with $q = \pi/a$ where a is the Nb-Nb intrachain separation. Weak scattering from the T_{2g} optical phonon near 150 cm^{-1} is observed in the T_{2g} spectrum. When the sample is immersed in superfluid helium at 1.8 K new peaks appear at 40–50 cm^{-1}, close in energy to 2Δ, which is ~54 cm^{-1} from tunneling measurements.[11] The position, width, and intensity of the new peaks are symmetry dependent, with E_g, T_{2g}, and A_{1g} components.

Earlier Sooryakumar and Klein[12] observed new Raman peaks close to 2Δ in superconducting $2H$-$NbSe_2$ and presented evidence that these peaks acquired their Raman activity by coupling to nearby Raman-active CDW phonons.[12-14] Two theoretical models for this coupling have been proposed.[15,16] However, in our case, the presence of the new peaks is not dependent on the existence of CDW phonons, since only the E_g phonon is of that type. Furthermore, the presence of the A_{1g} component and the absence of any Raman-active A_{1g} phonons demonstrate that the gap excitations have a direct Raman activity of their own.

We have also studied a single-crystal sample of V_3Si ($T_c = 16.9$ K, RRR = 15, $2\Delta \sim 41$ cm^{-1})[11] which is not believed to undergo a martensitic transformation. The E_g phonon appears near ~275 cm^{-1} with an intensity of ~1.5 counts/s. The T_{2g} phonon is unobservable. At 1.8 K new peaks, similar to the A_{1g} spectrum of Nb_3Sn in Fig. 1(c), appear at ~40 cm^{-1} with an intensity of ~3.5 counts/s. Only E_g and A_{1g} components of the 2Δ peak are observed; the T_{2g} peak is absent. Hackl, Kaiser, and Schicktanz[17] recently reported similar results on martensitically transforming V_3Si, including a study of the temperature dependence.

In a light-scattering experiment in metals, $q_\parallel$, the component of the transferred wave vector $\vec{q}$ parallel to the surface, is conserved. For our experiments $q_\parallel = 1.2\times 10^5$ cm^{-1}. The perpendicular component $q_\perp$ is not conserved but is spread about zero with a width given by $1/\delta$. The light-scattering event creates an electron-hole pair with respective wave vectors at, say $\vec{k}+\vec{q}$ and $\vec{k}$. In the normal state the excitation energy is $\epsilon_{k+q} - \epsilon_k \approx \vec{v}_k \cdot \vec{q}$, where ϵ_k is the Bloch energy and where $\vec{v}_k$ is the group velocity at $\vec{k}$ on the Fermi surface. In the superconducting state electrons and holes become mixtures of quasiparticles, and the electron-hole pair spectrum acquires a threshold at the local gap $2aW_k$. The spectrum depends on whether the characteristic frequency $\omega_c = qv$ is large or small compared with 2Δ. Here v and Δ are averages of v_k and Δ_k over the Fermi surface. Since $\xi_0 = v/2\Delta$, this is equivalent to ξ_0 being large or small compared to δ. For Nb_3Sn and V_3Si $\omega_{c\parallel} = q_\parallel v$ is 4–5 cm^{-1}, and $\omega_{c\perp} = v/\delta$ is 25–30 cm^{-1}.[18] Thus, the two A-15 samples are probably in the "intermediate-q" limit ($qv \sim \Delta$), at least for an average electron in these complex materials.

Abrikosov and Fal'kovskii[1] calculated the zero-temperature Raman spectrum in the large-q limit ($qv \gg 2\Delta$) using the BCS theory. The scattered intensity I_s shows a turnon and an overshoot: It rises discontinuously from zero to $\pi/2$ times the normal-metal result (I_n) at $\omega = 2\Delta$ and then continuously approaches $I_n \propto \omega$ from above as ω increases above 2Δ.[2] Abrikosov and Genkin[3] later showed that when the theory is corrected for Coulomb polarization effects the shape of I_s is the same but the Coulomb interaction screens the average matrix element for light scattering, leaving only the fluctuation $\delta M_k^{ij} = M_k^{ij} - \langle M^{ij}\rangle$. Here M_k^{ij} is the overall matrix element for scattering of light from polarization i to j with creation of an electron at $\vec{k}+\vec{q}$ and a hole at $\vec{k}$. It is closely related to the inverse effective-mass tensor $(m_k^{-1})^{ij}$. $\langle M^{ij}\rangle$ is the Fermi-surface average of M_k^{ij}.

In the small-q case screening produces a similar result, but the spectrum is different, having a true peak at 2Δ, rather than a turnon and overshoot.[19] When vertex and Coulomb corrections are made, a nonconstant M_k leads to a response function $B_\Gamma(\omega)$ for each symmetry that is nonzero at frequencies of order 2Δ and is given approximately by[19]

$$B_\Gamma(\omega) = -2N(0)\langle f_k |\delta M_k^\Gamma|^2\rangle, \tag{1}$$

$$f_k = \beta_k^{-1}(1-\beta_k^2)^{-1/2}\arcsin\beta_k, \tag{2a}$$

$$\beta_k = \omega/(2\Delta_k), \tag{2b}$$

where $N(0)$ is the density of states for one spin. For A_{1g}, E_g, and T_{2g} symmetry, we have for

TABLE I. Summary of results.

	Nb$_3$Sn $\Delta_0 \pm \sigma$ (cm^{-1})	$2\Delta_0/kT_c$	$2\Delta/kT_c$ [a]	V$_3$Si $\Delta_0 \pm \sigma$	$2\Delta_0/kT_c$	$2\Delta/kT_c$ [a]
E_g	20.6 ± 4.2	3.3	4.2–4.4	20.0 ± 2.4	3.4	3.4–3.6
A_{1g}	26.0 ± 4.8	4.2		Seen, weak		
T_{2g}	25.0 ± 3.4	4.0		Not seen		

[a] Tunneling results from Ref. 11.

$|\delta M_k{}^\Gamma|^2$

$$|\delta M_k{}^A|^2 = \tfrac{1}{3}|\mathrm{Tr}\,\delta M_k|^2, \tag{3a}$$

$$|\delta M_k{}^E|^2 = \tfrac{1}{6}\sum_{i<j}|M_k{}^{ii} - M_k{}^{jj}|^2, \tag{3b}$$

$$|\delta M_k{}^T|^2 = \tfrac{1}{3}\sum_{i<j}|\delta M_k{}^{ij}|^2. \tag{3c}$$

The corrections to Eq. (1) are small for small gap anisotropy. They vanish for the BCS case $\Delta_k = \text{const}$ and for $\Gamma = E_g$ or T_{2g}.[19]

One can show that the Raman cross section for each symmetry is proportional to $-\mathrm{Im}B_\Gamma(\omega + i0^+)$, which can be written as

$$-\mathrm{Im}B_\Gamma(\omega) = 4\pi\langle|\delta_M{}^\Gamma|^2\rangle N(0)\int_0^{\omega/2}\frac{P_M{}^\Gamma(\Delta)\Delta^2 d\Delta}{\omega(\omega^2 - 4\Delta^2)^{1/2}}, \tag{4a}$$

where

$$P_M{}^\Gamma(\Delta) = N(0)^{-1}\textstyle\sum_k \delta(\Delta_k - \Delta)\delta(\epsilon_k) \times |\delta M_k{}^\Gamma|^2\langle|\delta M^\Gamma|^2\rangle^{-1} \tag{4b}$$

is a weighted distribution function for the gap Δ_k. This theory implies that observation of direct electronic Raman scattering requires anisotropy in the matrix element M_k.[3]

The smooth solid line in Fig. 1(c) is a least-squares fit using Eqs. (4a) and (4b) with a Gaussian for $P_M{}^\Gamma(\Delta)$. For the E_g and T_{2g} spectra from Nb$_3$Sn the fits also included a phonon contribution and a linear background attributed to interband electronic excitations.[9,10] Their individual contributions are shown by the lower solid curves in Fig. 1(d). The one with a peak near 50 cm^{-1} is from Eqs. (4a) and (4b). The phonon contribution gives the curve with the 175-cm^{-1} peak whose width is attributed to interband electronic decays.[10] This and the linear electronic background are given the turnon and overshoot behavior near 50 cm^{-1} expected for intraband Raman scattering in the large-q limit. (An interband process can be treated as an intraband umklapp process.) A Gaussian distribution of Δ_k's was used for all these curves.

The results of the fits are compared to tunneling results[11] in Table I. Δ_0 is the mean and σ the standard deviation of the Gaussian used for $P_M(\Delta)$. It appears that the weighting in the E_g spectrum favors the lower part of the distribution of Δ_k's, compared with the A_{1g} and T_{2g} weighting. According to Eq. (3b), the E_g spectrum comes mainly from those parts of the Fermi surfaces where $|M_k{}^{ii} - M_k{}^{jj}|^2$ is largest. Assuming $M_k{}^{ij} \sim (m_k{}^{-1})^{ij}$, and looking at the Fermi surface calculated by Mattheiss and Weber for Nb$_3$Sn,[20] we note that $|(m_k{}^{-1})^{ii} - (m_k{}^{-1})^{jj}|^2$ will be large around the necks of the $e_{20}(\Gamma)$ sheet. We therefore speculate that the gap on these necks is about 20% less than the average gap.

For simplicity and brevity, the theory and fits were confined to either the small-q or large-q limit. We have also performed calculations in the more complicated intermediate-q case.[19] As $qv/2\Delta$ becomes greater than 1, the 2Δ peak broadens and weakens but maintains its peaked character until $qv/2\Delta \gtrsim 10$. The small-q approximation employed in the fits to the data somewhat overestimates the real σ but is not in serious error.

In conclusion, we have seen Raman peaks at 2Δ in Nb$_3$Sn and V$_3$Si due to direct coupling of light to superconducting electrons. This implies an anisotropic Raman matrix element. In Nb$_3$Sn the symmetry dependence of the observed values of Δ_0 implies a reasonably large (~20%) gap anisotropy.

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Chaotic Noise Observed in a Resistively Shunted Self-Resonant Josephson Tunnel Junction

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The current-voltage characteristics of Josephson tunnel junctions shunted by a resistance with a substantial self-inductance exhibit stable negative-resistance regions. Very large increases in the low-frequency voltage noise with temperatures of 10^6 K or more observed near these regions arise from switching between subharmonic modes. Moderate increases in the noise, with temperatures of about 10^3 K, arise from chaotic behavior. These results are substantiated by analog and digital simulations.

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Huberman, Crutchfield, and Packard[1] were the first to point out that a resistively shunted Josephson junction with appropriately chosen parameters should exhibit chaotic behavior when driven by an external rf field. Subsequently, other authors[2-6] have developed and extended this work using simulations. Apart from the inherent interest in chaotic behavior, these ideas may be highly relevant to the design of devices based on the Josephson effect; for example, it is likely that the large levels of excess noise observed in parametric amplifiers[7-9] were due to chaos. We have chosen to study possible chaotic effects in a different system, consisting of a Josephson tunnel junction with capacitance C shunted by a resistance R with a self-inductance L. In experiments on many