Such strong coupling is a consequence of the large volume of k space filled by the undulating cylinder $|E_i(\vec{k}) - E_j(\vec{k}) - E_1| \lesssim \epsilon_1$.

The phonon hyperfine structure appears to be unusually sensitive to changes in thickness of surface film. Lukeš and Schmidt[1] find that increasing the Ge film thickness from 37 Å to 48 Å enhances edges corresponding to $n = 0, \pm 1$, but tends to suppress other edges. The bulk Ge absorption length here is 50 Å. This anomalous sensitivity may be due to spatial dispersion.[19] Because excitons are formed, there are two normal modes of mixed photons and excitons for transverse electromagnetic waves. These are coherent, and their interference after reflection from the uneven bulk surface into the film affects the degree to which exciton-phonon hyperfine structure is observable in the external reflectance.

Dynamically unstable excitons, like hydrogenic excitons, may annihilate and emit photons and phonons. They may also emit photons and phonons by scattering, as hot electrons do. Finally, they may decay directly into free electrons and holes. We believe this to be the first positive identification of excitons which overlap the electron-hole scattering continuum.

---

*Guggenheim Fellow assisted by a Sloan grant on leave from the Department of Physics, University of Chicago, Chicago, Illinois.

[1]F. Lukeš and E. Schmidt, Phys. Letters 2, 288 (1962): Ge, GaSb.

[2]F. Lukeš and E. Schmidt, 1962 Semiconductor Conference (Institute of Physics, London, 1962), p. 389: Si, InSb, InAs, GaAs.

[3]L. H. Hall, J. Bardeen, and F. J. Blatt, Phys. Rev. 95, 559 (1954).

[4]D. Brust, J. C. Phillips, and F. Bassani, Phys. Rev. Letters 9, 94 (1962).

[5]D. Brust (to be published), in which hyperbolic arcs obtained by sectioning these surfaces with symmetry planes are given.

[6]H. Y. Fan, Rept. Progr. Phys. 19, 114 (1956).

[7]J. C. Phillips, Phys. Rev. 113, 151 (1959).

[8]B. N. Brockhouse and P K. Iyengar, Phys. Rev. 111, 747 (1958).

[9]B. N. Brockhouse, Phys. Rev. Letters 2, 256 (1959).

[10]We have discussed hyperfine structure in $\epsilon_2(\omega)$ whereas the measured structure occurs in the reflectance R. Whether the hyperfine structure in ϵ_2 will be reproduced in R depends on the relative variation of ϵ_1 and ϵ_2 near the M_1 edge. To see that no general statement can be made, it is sufficient to note that the phonon hyperfine structure is nearly absent[2] from $\Lambda_3(m_J = \frac{3}{2}) \rightarrow \Lambda_1$ but is quite evident in $\Lambda_3(m_J = \frac{1}{2}) \rightarrow \Lambda_1$. In the particular case of the M_1 edge shown in Fig. 1, one finds $(d\epsilon_2/d\epsilon_1)_- = 5$, while $(d\epsilon_2/d\epsilon_1)_+ = \frac{1}{2}$. This means that one-phonon absorption (-) hyperfine edges can appear larger than the corresponding emission (+) edge, and this is indeed seen to be the case.

[11]J. M. Rowell, P. W. Anderson, and D. E. Thomas, Phys. Rev. Letters 10, 334 (1963).

[12]J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, Phys. Rev. Letters 10, 336 (1963).

[13]Y. Toyozawa, Suppl. Progr. Theoret. Phys. (Kyoto) 12, 111 (1959).

[14]M. Cardona and G. Harbeke, Phys. Rev. Letters 8, 90 (1962).

[15]D. T. F. Marple and H. Ehrenreich, Phys. Rev. Letters 8, 87 (1962).

[16]M. A. Lampert, Phys. Rev. 97, 352 (1955).

[17]D. Brust, M. L. Cohen, and J. C. Phillips, Phys. Rev. Letters 9, 389 (1962).

[18]It is easy to see from phase-space arguments and the virial theorem that the effect of the real part of the electron-hole Coulomb self-energy $\Sigma_1(E)$ is to sharpen M_1 edges and blur M_2 edges. This may explain why no M_2 edges have yet been clearly resolved.

[19]S. I. Pekar, reference 2, p. 419.

SHAPE RESONANCES IN SUPERCONDUCTING THIN FILMS*

John M. Blatt and Colin J. Thompson
Courant Institute, New York University, New York, New York
and Applied Mathematics Department, University of New South Wales, Kensington, Australia
(Received 26 February 1963)

The basic equations for superconductors[1] are usually written for an infinite, homogeneous medium. We have set up the corresponding equations for a slab with thickness a, and solved them numerically for various slab thicknesses. The equations take into account, in a self-consistent fashion, the Coulomb potential generated by the charge density of the electrons plus an assumed uniform background of positive charge. The boundary condition on the electron wave functions is that they vanish at the faces of the slab.

One rather expects resonance effects whenever an energy level $\eta_n(a)$, for motion perpendicular to the slab faces, passes through the Fermi surface as the thickness a is varied. What is surprising, however, is the size of the resonance ef-

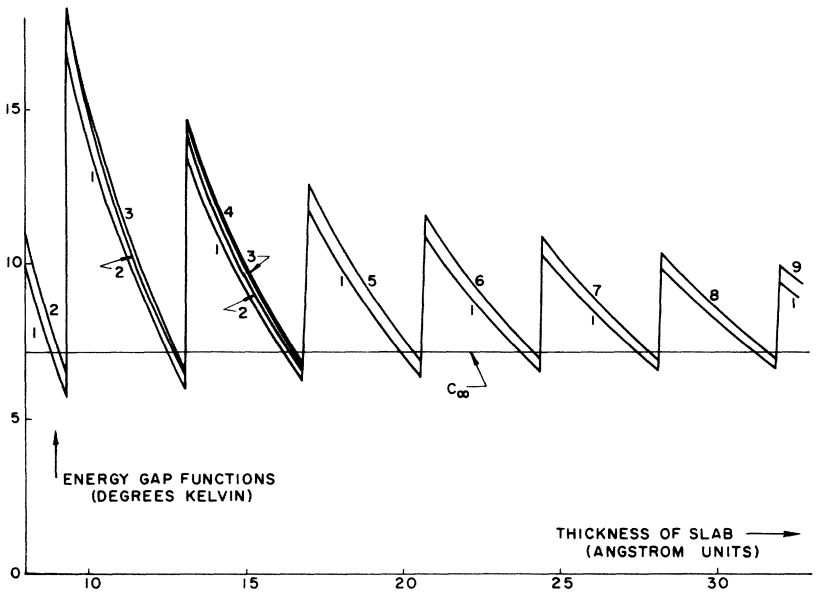

FIG. 1. Superconducting energy gap parameters C_n, vs thickness of film. At each resonance, a new value of n starts to contribute. All values of C_n are shown for small thicknesses; thereafter, only the largest and smallest C_n are shown, to avoid confusion. The peak heights lie well above the bulk value, C_∞, which is also shown on the figure. The troughs are only slightly below C_∞. The width of the resonances is too small to show on the scale of this figure. The distance between resonances equals one half of the deBroglie wavelength of an electron at the Fermi surface. The parameters used for this figure were $N/V = 2 \times 10^{22}$ electrons/cm^3, $\rho = 0.3$, and $\hbar\omega_c = 100°$K.

fect in the energy gap parameter C_n, see Eq. (2) below, as shown for a typical case in Fig. 1. We see that there is an increase by more than a factor of 2 for the first few resonances, and although the size of the resonances decreases as the slab is made thicker, the decrease is quite slow, roughly inversely proportional to the width of the slab.

The rise in the energy gap values C_n is too steep to show on the scale of Fig. 1. In Fig. 2, we have plotted detail for one of the resonances (near $a = 13$ Å). The new energy gap value, C_4, comes suddenly when $\eta_4 - \mu = +\hbar\omega_c$, the usual cutoff energy. Initially, C_4 lies below the others, but it rises above the other three C values by the time $\eta_4 - \mu = -\hbar\omega_c$; beyond this point, the curves become flat on the scale of Fig. 2. Some of the sharpness is due to the sharp cutoff in the model interaction, but the resonance effect itself should not depend on details of the interaction.

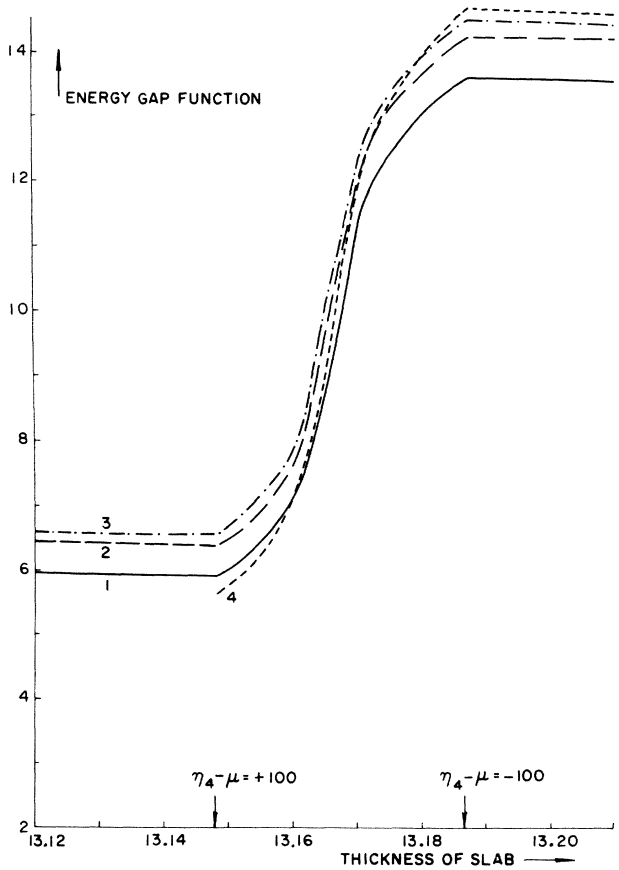

FIG. 2. One of the resonances of Fig. 1, shown on an expanded scale. The new gap value, C_4 in this case, appears when $\eta_4 - \mu = +\hbar\omega_c$, and rises above the other three values by the time $\eta_4 - \mu = -\hbar\omega_c$. The variation of the C_n with slab thickness a outside the resonance region itself is too small to show on the scale of this figure, i.e., the sloping curves of Fig. 1 appear as horizontal straight lines in the present figure.

The energy gap parameters $C_{\vec{k}}$ are highly "anisotropic" in this theory: The index $\vec{k}$ breaks up into three indices (n, k_2, k_3), corresponding to motion in the x, y, and z directions. n is a discrete index, k_2 and k_3 are quasi-continuous with the usual periodic boundary conditions in the y and z directions. The energy $\epsilon_{\vec{k}}$ is related to η_n by

$$\epsilon_{\vec{k}} = \eta_n + (\hbar^2/2m)(k_2^2 + k_3^2). \quad (1)$$

The energy gap parameters $C_{\vec{k}}$ have the form

$$C_{\vec{k}} = C_n \text{ (independent of } k_2, k_3) \quad \text{for } |\epsilon_{\vec{k}} - \mu| < \hbar\omega_c, \quad (2a)$$

$$= 0 \quad \text{for } |\epsilon_{\vec{k}} - \mu| > \hbar\omega_c. \quad (2b)$$

The simple form (2), which greatly simplifies the numerical solution, is associated with the usual simplified model interaction, i.e., constant matrix elements for $|\epsilon_{\vec{k}} - \mu| < \hbar\omega_c$, zero outside that region.

For any given finite width a of the slab, only a finite number of eigenvalues η_n contribute; values of η_n in excess of $\mu + \hbar\omega_c$ give zero, because then all the $\epsilon_{\vec{k}}$, as given by Formula (1), lie outside the interaction region. It is this feature of the problem which permits a straightforward, though not terribly simple, machine calculation.

Returning to the results, it should be noted that the resonances are not symmetrical about the bulk value of C, which is also indicated on Fig. 1. The peaks are much higher than the bulk value, whereas the troughs are only slightly below the bulk value. It is possible, therefore, that some average effect remains even for films of nonuniform thickness.

The distance between resonances in Fig. 1 is one half of the deBroglie wavelength for an electron at the Fermi surface. The precise positions of the resonances are sensitive to the boundary conditions imposed, and should not be taken literally; but the distance between resonances is independent of boundary conditions at the surface. The transition region, near the surface, is only some 2Å thick for our self-consistent solutions.

We believe it to be highly likely that similar resonances occur also in other geometries; for example, there might be size resonances in the nuclear pairing energy.

We would like to express our thanks to Dr. P. W. Anderson and Dr. J. N. Lyness for valuable discussions; we are grateful to the Courant Institute, New York University, to the U. S. Atomic Energy Commission, and to the U. S. Air Force for assistance and support for this research.

*The work presented in this paper is supported by the AEC Computing and Applied Mathematics Center, Courant Institute of Mathematical Sciences, New York University, New York, New York, under Contract AT(30-1)-1480 with the U. S. Atomic Energy Commission; it is also supported by a research grant from the U. S. Air Force to the University of New South Wales, Kensington, New South Wales, Australia.

[1]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957); N. N. Bogoliubov, V. V. Tolmachev, and D. V. Shirkov, Fortschr. Physik 6, 605 (1958).

IMAGE OF THE PHONON SPECTRUM IN THE TUNNELING CHARACTERISTIC BETWEEN SUPERCONDUCTORS

J. M. Rowell, P. W. Anderson, and D. E. Thomas
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received 14 March 1963)

The equation for the energy gap function $\Delta(E)$ in a superconductor, using the Eliashberg[1] phonon interaction between electrons, predicts that $\Delta(E)$ will exhibit structure at energies determined by the phonon energies, specifically at the energy gap Δ plus multiples of the phonon frequencies[2] (assuming an Einstein phonon spectrum). It is evident that structure in the energy gap function $\Delta(E)$ will be reflected in the conductance vs voltage plot for a metal-insulator-superconductor tunnel junction, since the conductance is proportional to the density of states.[3] Structure in lead which can be related to the phonon spectrum has been reported by Giaever[4] and structure at phonon harmonics, also in Pb, by Rowell, Chynoweth, and Phillips.[5]

Considerable refinement in experimental technique has allowed us to make a much more detailed quantitative study of this phenomenon. This and the next Letter report the following develop-