ADVANCES IN PHYSICS, 1981, VOL. 30, NO. 5, 677–695

Are there acoustic plasmons?

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[Received 30 June 1981]

ABSTRACT

A survey of theoretical research on acoustic plasmons is given and prospects for the observation of these elusive modes are examined. Possible acoustic plasmon contributions to the transition temperatures of the superconducting A-15 compounds are considered. Directions for future experiments and theory are suggested.

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§ 1. INTRODUCTION

In the collective motion of a system of two types of electronic carriers in a solid, differing in effective mass, those of lesser mass are effective in screening the Coulomb interaction between those of greater mass, thus reducing the range of the coupling. There can result an oscillatory mode at low frequency referred to as an acoustic plasmon. To visualize the respective charge displacements consider a system with both s- and d-electrons, with effective masses $m_d \gg m_s$. Relative to the positive charge background, the displacement of the s-electrons is u_s and that of the d-electrons, u_d. The electrostatic field resulting from these displacements (fig. 1) produces restoring forces and the following equations of motion apply :

$$n_s m_s \ddot{u}_s = -4\pi e^2(n_s^2 u_s + n_d^2 u_d), \tag{1 a}$$

$$n_d m_d \ddot{u}_d = -4\pi e^2(n_d^2 u_d + n_s^2 u_s), \tag{1 b}$$

where n_s and n_d represent the densities of s and d electrons. Assuming solutions of the form $u \sim \exp(i\omega t)$ gives the eigenvalue criterion

$$\omega^2\left(\omega^2 - \frac{4\pi n_s e^2}{m_s} - \frac{4\pi n_d e^2}{m_d}\right) = 0. \tag{2}$$

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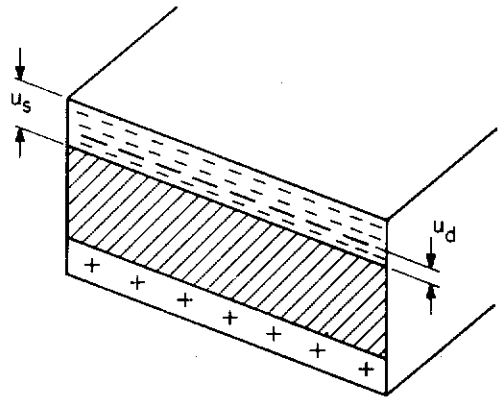
Fig. 1



Schematic illustration of the charge displacement u_s for the lighter electrons and u_d for the heavier d-electrons relative to the charged positive background. The shaded region is neutral, and the restoring forces yield acoustic plasmon oscillations in addition to the conventional one-component plasma oscillation.

For a single species of electron ($m_d \to \infty$) the conventional plasma oscillation frequency,

$$\omega_{\mathrm{pl},s}{}^2 = 4\pi n_s e^2/m_s \tag{3}$$

is obtained. Introducing the second species causes this 'optic' plasmon frequency to be shifted and, in addition, the zero-frequency mode allowed for by eqn. (2) occurs; this has the relative amplitudes and phases that correspond to the vanishing of the net electron restoring force. It is the $k \to 0$ acoustic plasmon.

Theoretical investigations of the damping and the low-energy dispersion of acoustic plasmons over the past 25 years generally suggest that such modes should exist under appropriate conditions, as well-defined excitations in doped semiconductors and in some transition-metal compounds. Nevertheless, there will be scepticism about the existence of these plasma excitations so long as there is no direct experimental evidence for them. There appear to be few experimental efforts to search for these elusive, but potentially important, excitations.

The purpose of the present article is to review the conditions necessary for the formation of well-defined acoustic plasmon modes, and to examine their accessibility to experimental probes. And the possibility that these modes may provide a mechanism for superconductivity, in particular in the controversial A-15 transition metal compounds, is examined at some length.

Pines originally suggested that acoustic plasmons could exist [1]. In the idealized situation where the light electron screening is represented by the Thomas–Fermi approximation, the acoustic plasmon dispersion is given by [2]

$$\Omega^2 \cong \frac{m_s v_{\mathrm{F}s}{}^2 k^2}{m_d}, \tag{4}$$

where v_{Fs} is the Fermi velocity of the s-electrons. Hence the ' plasmon sound ' velocity is a fraction of v_{Fs}, but generally higher than phonon velocities by an order of magnitude. Unfortunately this is a surprisingly awkward range of energy and momentum to sample experimentally.

Damping of the acoustic plasmon occurs by Landau decay into the s electron–hole continuum. Consequently early emphasis was placed on semiconductors where the electron densities and masses could be varied by doping. But relatively short electron relaxation times [3] can then be associated with scattering by defects and impurities introduced in the doping process, so that the prospects of such modes having narrow energy widths are then marginal.

Perhaps the strongest motivation for pursuing the study of the elusive plasmons has been their potential role as a mechanism for superconductivity. The BCS theory of superconductivity [4] is based on the role of electron–phonon interactions in pairing electrons. Experimentally, the theory is confirmed in fine detail for many materials. The superconducting transition temperature is given by

$$T_c \simeq 0{\cdot}7\theta_D \exp\left(-\frac{1+\lambda}{\lambda-\mu^*}\right), \tag{5}$$

in the strong coupling version of the theory, where θ_D is a Debye temperature for the phonon spectrum, λ is the effective electron–electron pairing parameter arising from phonon exchange, and μ^* reflects the influence of the competing Coulomb repulsion. Typical values of $\lambda \simeq 1$, $\mu^* \cong 0{\cdot}1$ and $\theta_D \simeq 300\,\mathrm{K}$ correspond to known high temperature superconductors; it is generally agreed that the phonon-exchange mechanism is not likely to give a T_c greater than 25 K. At first glance, the exchange of an acoustic plasmon, rather than a phonon, by a pair of electrons would be a promising mechanism for superconductivity, in view of the higher prefactor $\theta_{pl} \sim 3000\,\mathrm{K}$, which raises the possibility of a room temperature superconductor [5]. An early investigation by Garland [6] concluded that a system of d- and s-electrons could admit superconductivity in a transition metal even in the absence of electron–phonon coupling, although he did not mention acoustic plasmons which at that time were envisaged in the context of Bi and other semimetals [7]. The search for high temperature superconductors received impetus from the suggestion of Little [8] that mechanisms involving relatively high-frequency excitonic states might be highly favourable to enhanced T_c values, and the general problem of electronic mechanisms for superconductivity was subsequently treated in a series of articles by groups in the Soviet Union, with the acoustic plasmon role considered first by Geilikman [9]. Independently, Fröhlich demonstrated that the electron–phonon interaction should decrease with the electronic bandwidth (contrary to widely held belief), and thus the alternative acoustic plasmon mechanism may be particularly relevant to transition metals [10]. The formal similarity of excitonic and plasmon mechanisms in high temperature superconductivity has been emphasized by Ginzburg [11].

Early attempts to infer the existence of acoustic plasmons in specific transition metals were not convincing. Rothwarf [12] suggested that low-lying acoustic plasmons could dramatically modify the low temperature

thermodynamic properties such as the specific heat, but the sparse experimental data was equivocal on this issue. The phonon spectra of transition metals are complex enough to mask any influence of higher-energy plasmon modes. An attempt [13] to attribute the anomalous phonon dispersion in Nb to a hybrid acoustic plasmon effect is tenuous, especially since the Nb energy bands do not exhibit the overlapping electron structure required for acoustic plasmons.

Semiconductors and semi-metals [14] have received wide attention but, to date, the only candidate observation of acoustic plasmons is the Raman scattering [15] from doped silicon which has a form suggestive of an overdamped low-energy electronic excitation. Nevertheless the possibility to change electron densities in doped semiconductors has stimulated theoretical speculations about how one might achieve high-temperature superconductors. Various methods applied to this problem claim $T_c \sim 100$ K as attainable at realistic electron densities [16–18].

Transition metal compounds have received more detailed analysis as the use of modern computers has led to a better understanding of their electronic structure. The high-T_c materials of the A-15 structure are particularly inviting since there is a lack of an isotope effect in T_c [19] and various other experimental features [20] are anomalous. In a thorough analysis of a model with tight-binding d-electrons embedded in a modified free-electron system, Gutfreund and Unna [21] observed that the energy bands of V_3Ga were well suited to the existence of acoustic plasmons, and independently, Kahn and co-workers [22–24] have considered the exchange of acoustic plasmons as an alternative mechanism for superconductivity in the A-15 compounds.

Other manifestations of acoustic plasmons might be found in optical studies, as in the case of the mixed valence compound SmS [25], or in the anomalous dependence of the superconducting transition temperature on structure and carrier density as in the alkali tungsten bronzes [26].

Finally we remark on the vital role of the electron relaxation time and of the plasmon coupling to the local field of the lattice vibrations. In the phonon energy range strong hybridization with phonons may yield a distortion of the acoustic plasmon branch [27] which may have a bearing on the coupling to electromagnetic probes. To allow observability in this range of energy, the sample purity of the transition metal compounds would have to be exceptionally good. A case in point is the peculiar and dramatic drop in the superconducting transition temperature of the A-15 compounds subjected to various types of disorder [28, 29]. The universal depression of T_c as a function of the residual resistivity of the damaged compounds exhibits a close correlation with a simple criterion for damping of the acoustic plasmons in these materials [30].

In summary, the existence of acoustic plasmons has clear support from the theoretical studies but there is a need for further guidance for the direction to be taken in experimental searches because acceptable damping conditions are not readily achieved in actual materials, and because the coupling of experimental probes to excitations with acoustic character in the 0·1 eV range is particularly difficult.

§ 2. Dielectric response formulation

Consider a two-component plasma with the states of the heavier electrons (or holes) labelled as d-states and the lighter as s-states, described by the Hamiltonian

$$H = \sum_k E_s(k) c_k^\dagger c_k + \sum_k E_d(k) a_k^\dagger a_k + H_{\text{int}}, \tag{6}$$

where the Coulomb interaction is

$$H_{\text{int}} = \sum_{q,k} \frac{4\pi e^2}{q^2} \rho_q \rho_{k-q}, \tag{7}$$

and the electron density operator is

$$\rho_q = \sum_p c_{p+q}^\dagger c_p + \sum_p a_{p+q}^\dagger a_p. \tag{8}$$

The $c_k^\dagger$ (c_k) represent creation (annihilation) operators of s-states and similarly the a_k operators describe d-electrons.

Collective oscillations of the system are determined by the dielectric response function

$$\epsilon(q, \omega) = \epsilon_0 + \epsilon_s(q, \omega) + \epsilon_d(q, \omega) + \epsilon_{sd}(q, \omega), \tag{9}$$

and its zeros correspond to the normal modes. An ordinary one-component plasma yields a large-frequency behaviour,

$$\epsilon(q, \omega) \cong 1 - \frac{\omega_{\text{pl}}^2}{\omega^2}, \tag{10}$$

with a well-defined plasmon excitation at $\omega = \omega_{\text{pl}}$ because the imaginary part of the dielectric function vanishes in the regime $qv_{\text{F}} \ll \omega_{\text{pl}}$.

The more general case of two carriers may be described by the standard formula,

$$\epsilon = \epsilon_0 + \frac{4\pi e^2}{q^2} \sum_{k,l,l'} |\langle \mathbf{k}, l | \mathbf{k}+\mathbf{q}; l' \rangle|^2 \frac{f[E_{l'}(\mathbf{k}+\mathbf{q})] - f[E_l(\mathbf{k})]}{\omega - E_{l'}(\mathbf{k}-\mathbf{q}) + E_l(\mathbf{k}) + i\delta}, \tag{11}$$

where $f[E_l(\mathbf{k})]$ denotes the Fermi occupation factor, l, l' are band indices, and the matrix element indicates the overlap of Bloch wavefunctions designated by $|\mathbf{k}, l\rangle$. Generally, two branches in the plasmon spectrum will occur. One will be a modified ' optical ' mode with a frequency defined by $\omega_{\text{pl}}^2 = \omega_s^2 + \omega_d^2$ in the long wavelength limit, where $\omega_s^2 = 4\pi n_s e^2/m_s$ and $\omega_d^2 = 4\pi n_d e^2/m_d$. The second, lower-energy, branch will usually be overdamped because of its strong decay into the electron–hole continuum. However, under exceptional circumstances the lower energy d-electron plasmon will be shifted above the d-electron continuum by virtue of the screening by s-electrons, and hence may exist as a reasonably well-defined excitation.

A straightforward demonstration of the acoustic character of the low energy plasma mode is to consider the dielectric function in the limit $m_d \gg m_s$. The screening by the s-electrons is represented by the Thomas–Fermi approximation according to

$$\epsilon_s \cong \frac{K^2}{q^2}, \quad \text{for } qv_{\text{F}s} > \omega, \tag{12}$$

where $K^2 = 3\omega_s^2/v_{Fs}^2$ defines the screening wave vector. The energy regime of interest is above the d-electron continuum where the d-state dielectric function is

$$\epsilon_d \cong -\frac{\omega_d^2}{\omega^2}, \quad \text{for } qv_{Fd} < \omega. \tag{13}$$

Adding eqns. (12) and (13) immediately gives the acoustic plasmon energy as a function of momentum (' acoustic ' since $\Omega \to 0$ as $q \to 0$)

$$\Omega \cong sq \equiv \frac{\omega_d v_{Fs}}{\omega_s \sqrt{3}} q. \tag{14}$$

In a pure material, the acoustic plasmon will have an *intrinsic* lifetime τ_L from the possible Landau decay into the s-electron continuum. This process can be estimated from the imaginary part of the dielectric function in the effective mass approximation which gives

$$\frac{1}{\tau_L} = \frac{\pi \omega_d^2}{4 v_{Fs} K} q. \tag{15}$$

Therefore the ratio of the acoustic plasmon width to its energy is roughly independent of momentum and gives the following simple condition for weakly damped plasmons :

$$\Omega \tau_L = \frac{4}{\pi} \left(\frac{3 m_d n_s}{m_s n_d} \right)^{1/2} \gg 1. \tag{16}$$

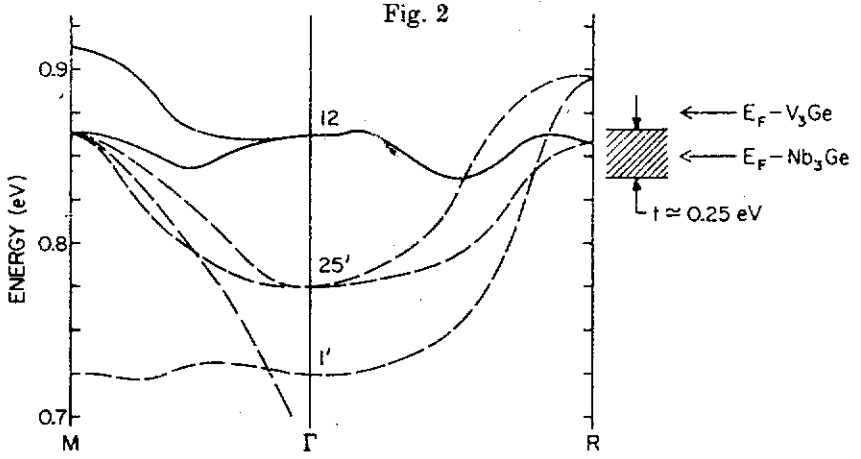
Although this versatile condition is readily achieved in doped semiconductors, there is additional damping due to impurity scattering and this presents a serious constraint.

A minor modification of the d-electron energy spectrum to allow a shift of the energy to $E_d = \Delta + k^2/2m_d$ allows for a significant improvement in flexibility of choice of the parameter to achieve optimum damping. Such a model was examined by Gutfreund and Unna [21], and was shown to give an adequate representation of the dielectric function of more complicated tight-binding energy band models including the case of V_3Ga. Furthermore, the qualitative features of the acoustic plasmon dispersion and damping are not sensitive to the interband matrix elements appearing in eqn. (11). A suggestive correspondence of the superconducting transition temperature with the energy band splitting Δ was found in the analysis of the alkali tungsten bronzes [26], where the dependence of T_c on crystal structure and alloy content was particularly anomalous.

A specific calculation of the dielectric response for the A-15 transition-metal compounds provides a realistic example of the acoustic plasmon formation. Recently a great deal of progress has been made in band-structure calculations for the high temperature superconductors [31, 32] such as Nb_3Ge with a $T_c = 23$ K. The computed band structure [31] for Nb_3Ge is shown in fig. 2 for the narrow energy region near the Fermi level E_F. The bands of Γ_{12} symmetry will be referred to as d-electrons and approximated by the tight-binding expression [20]

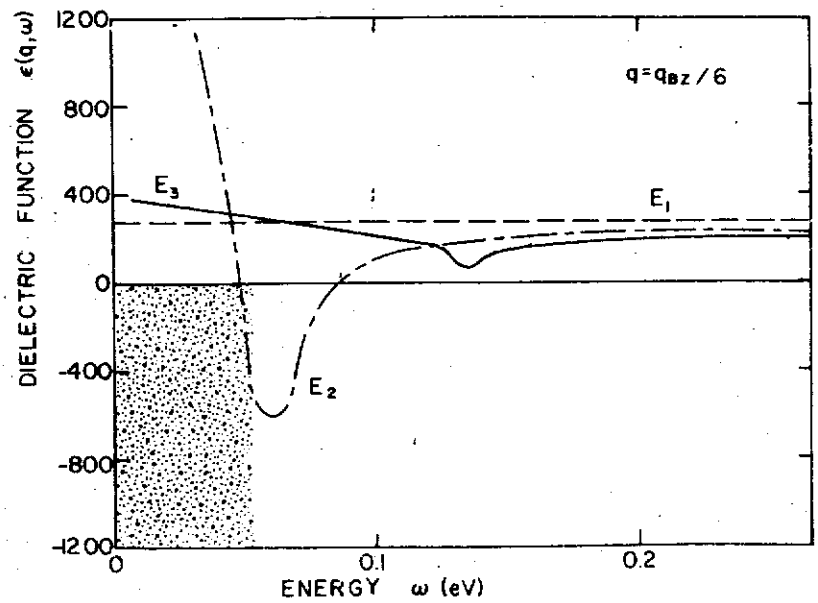
$$E_d = E_0 - A[\cos(ak_x) + \cos(ak_y) + \cos(ak_z)] + t[\cos(\tfrac{1}{2}ak_x)\cos(\tfrac{1}{2}ak_y) + \cos(\tfrac{1}{2}ak_x)\cos(\tfrac{1}{2}ak_z) + \cos(\tfrac{1}{2}ak_y)\cos(\tfrac{1}{2}ak_z)]. \tag{17}$$

Fig. 2



Band structure of Nb_3Ge as obtained by the APW computation of [31]. The narrow Γ_{12} band is referred to as the *d*-electron carrier, and the remaining bands ($\Gamma_{25'}$ and Γ_1, shown by dotted curves) are represented by an effective mass dispersion $E_s \simeq k^2/2m_s$. The intersection of the Fermi energy with the Γ_{12} symmetry band yields an acoustic plasmon throughout the shaded energy region including Nb_3Ge. Outside this range acoustic plasmons would not occur as illustrated by the Fermi energy of V_3Ge.

Fig. 3



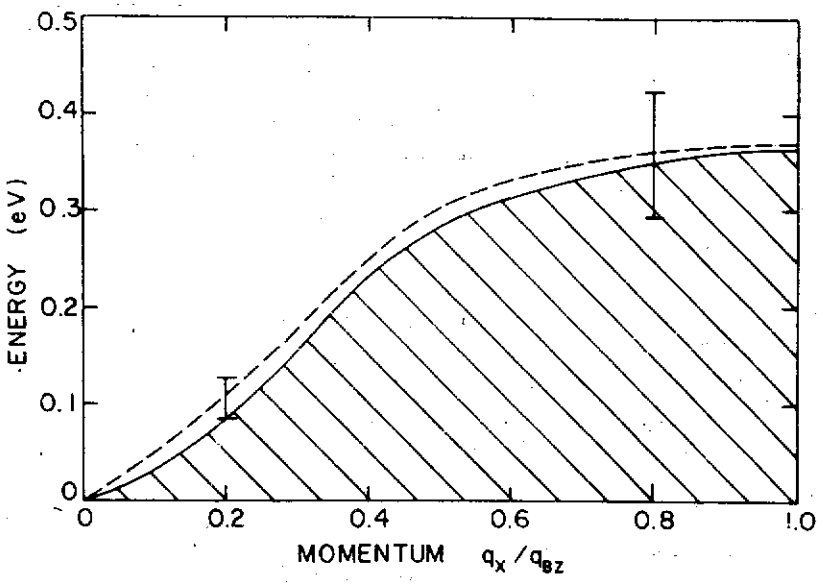
Real part of the total dielectric function $\epsilon = \epsilon_s + \epsilon_d$ as a function of energy. The acoustic plasmon zero occurs for a Fermi energy $E_F = E_2$ appropriate to Nb_3Ge. Whereas higher values of $E_F = E_1$ and, $E_F = E_3$ corresponding to Nb_3Sb and V_3Ge respectively have no acoustic plasmons. The shaded region is the *d* electron–hole continuum determined by a non-vanishing imaginary part of ϵ_d. A typical momentum of 1/6 of the Brillouin zone boundary is used here.

These d-electron states are distinguished from those in pure Nb, Ta, V and many transition metal compounds by their extremely narrow widths $t \simeq 0{\cdot}2$ eV. Approximating the broader bands of $\Gamma_{25'}$ and Γ_1 symmetry by the average effective mass m_s in the simplest approximation ($E_s \simeq k^2/2m_s$), Kahn and Ruvalds [22] have made numerical calculation of $\epsilon(q, \omega)$, using eqns. (11) and (17) for numerous A-15 compounds. The resulting dielectric function for $q = q_{BZ}/6$ is shown in fig. 3 for three selected values (E_1, E_2, E_3) for E_F. E_2 corresponds to Nb_3Ge (fig. 2) and the zero in $\epsilon(q, \omega)$ gives the energy of a well-defined acoustic plasmon ; E_2 is for V_3Ge, showing the failure of $\epsilon(q, \omega)$ to become negative in this energy range, thus disallowing an acoustic plasmon excitation ; E_1 corresponds to Nb_3Sb, for which the Γ_{12} band is effectively filled so that its d-electrons cannot yield acoustic plasmon oscillations.

Quantitative estimates of the acoustic plasmon damping also follow from the numerical model calculations. The resulting dispersion and width of the d-electron plasma oscillations for *pure* Nb_3Ge are shown in fig. 4. The acoustic plasmon branch remains close to the d electron–hole continuum with a width increasing at larger q in accordance with the effective mass model prediction of eqn. (15). The influence of defects, impurities and disorder are examined in the following section.

An interesting feature of these tight-binding calculations for the narrow band transition metal compounds is the extreme sensitivity of the acoustic plasmon branch to the placement of the Fermi energy E_F. If the narrow bands (of Γ_{12} symmetry in the A-15 example) are intersected by E_F, a well-defined mode exists. This situation is realized in Nb_3Ge, Nb_3Al, Nb_3Ga,

Fig. 4



Energy as a function of momentum showing the d-band continuum (shaded region), and the acoustic plasmon dispersion for parameters appropriate to Nb_3Ge. Note : 'error bars' indicate breadth due to Landau damping by decay into the s-states.

Nb_3Sn, Nb_3Si, V_3Si, V_3Ga and V_3Al, all of which happen to be rather good superconductors with high transition temperatures. By contrast the Fermi energy placement for V_3Ge, V_3Sn and Nb_3Sb will not yield acoustic plasmons.

§ 3. Superconducting compounds

A primary challenge for any proposal that acoustic plasmons can be responsible for superconducting electron pairing is to see how to distinguish the consequences of this process from those of the phonon-exchange process of the BCS theory. The recognition of the fundamental role of electron–phonon interactions dates back to the work of Fröhlich [33] and Bardeen [34], in which it was noted that superconductors tend to be poor normal conductors at room temperature, suggesting that scattering of electrons by thermally excited phonons is involved in superconductivity. The discovery of the isotope effect on the transition temperature T_c provided additional support for this even though the electron self-energy theories [33, 34] were not sustained in later years. In the BCS theory the phonon exchange processes give an effective attractive interaction strong enough to create bound electron pairs which leads to a superconducting state at temperatures below a transition temperature [35]

$$T_c \simeq 0{\cdot}7\theta_D \exp\left[-\frac{1+\lambda}{\lambda-\mu^*}\right], \tag{18}$$

where λ is the phonon-exchange pairing parameter, θ_D is a typical phonon energy of order 300 K, and the Coulomb repulsion between electrons is represented by

$$\mu^* \cong \frac{\mu}{1+\mu \ln (E_F/\theta_D)}, \tag{19}$$

where μ is the screened Coulomb interaction parameter. For Fermi energies of order of electron volts the Coulomb effect is small, say $\mu^* \simeq 0{\cdot}1$. Values for the BCS parameters can be independently estimated if the normal state resistivity $R(T)$ at high temperatures is known. The electron–phonon scattering gives

$$R \cong \frac{4\pi}{\omega_{pl}^2}\tau^{-1}, \tag{20}$$

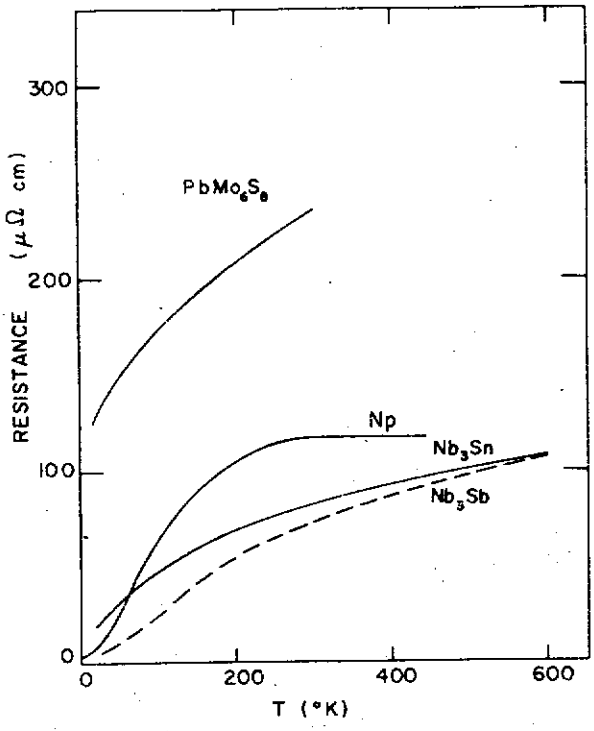
where

$$\frac{1}{\tau_{\text{phonon}}} \cong 2\pi\lambda T, \tag{21}$$

at temperatures $T > \theta_D$. Hence the measured temperature coefficient of resistivity yields a value for the coupling parameter λ. Quantitative confirmation for the BCS theory has been found for most superconducting materials in this way. An exception, which has caused spirited controversy, is the class of A-15 compounds, including Nb_3Ge with the highest known T_c of 23 K. The resistivity data for Nb_3Ge are compared to those for Nb_3Sb in fig. 5. These materials exhibit similar $R(T)$ slopes above 300 K but their disparate transition temperatures ($T_c \cong 1$ K for Nb_3Sb) would suggest an order of magnitude difference in λ. A thorough analysis of the optical data

for several A-15 compounds also demonstrates that typically these materials have resistivity slopes compatible with very small values of the electron–phonon coupling parameter $\lambda \simeq 0{\cdot}1$. This result is too small by a factor of at least 10 to account for the high T_c values of Nb_3Ge, V_3Si, etc.

Fig. 5



Resistivity as a function of temperature for the A-15 superconductors Nb_3Sn ($T_c = 18$ K) and Nb_3Sb ($T_c = 1$ K). By comparison the Chevrel phase compound $PbMo_6S_8$ exhibits a slope to the resistivity (hence larger electron–phonon coupling λ), and its higher value indicates a lack of saturation. Extrapolation of the high temperature region to zero is not a reliable indication of λ as demonstrated by the case of Np.

The most direct objection to the resistivity analysis is that ' saturation ', giving reduced slope, will occur when the electron mean-free-path approaches the atomic spacing [36]. However, the recent optical data of Yao and Schnatterly [37, 38] provide explicit evidence that mean-free-paths are longer than this (e.g. $l \sim 50$ Å at room temperature for V_3Si). Also, the superconductor $PbMo_6S_8$ exhibits [39] a much higher $\rho(T)$ (fig. 5) and yet has a slope compatible with a large value of λ (~ 1) consistent with its T_c. Nevertheless, the phonon-scattering contribution to resistivity should extrapolate to zero at $T = 0$, and the data in fig. 5 make it evident that other contributions, such as the electronic s–d scattering, must be taken into account in any analysis. A phenomenological ' parallel resistor ' formula has been applied in analyses

of the behaviour of the Nb_3Sn type shown in fig. 5 and, with appropriate values for the parameters, larger λ values are obtained [40]. But the same formula would suggest an extremely large value of λ (~ 4) for the Np data shown in fig. 5, whereas this metal is not superconducting at all.

It was originally believed that narrow bands (as are found in A-15 compounds) would imply high densities-of-states which in turn would lead to a large value for the electron–phonon parameter λ, which is given by [35]

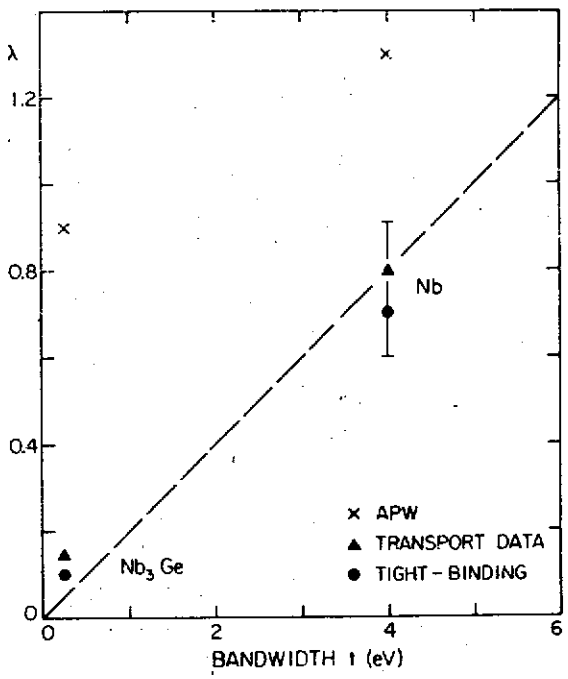
$$\lambda = N(0)\langle I^2\rangle / \langle \omega_q^2 \rangle M, \tag{22}$$

where $N(0)$ is the density of states at the Fermi level and

$$I_{\mathbf{k}\mathbf{k}'} = \hat{\boldsymbol{\epsilon}}_\alpha \cdot \langle \mathbf{k}' | \nabla U(\mathbf{r} - \mathbf{R}_l) | \mathbf{k} \rangle, \tag{23}$$

where $\hat{\boldsymbol{\epsilon}}_\alpha$ is the ion displacement for a phonon mode α, and $U(\mathbf{r} - \mathbf{R}_l)$ is the electron–ion potential and averages are taken over the electron Fermi surface. However, it is less well-known that the value of $\langle I^2 \rangle$ will tend to be *smaller* for narrow-bands. The tight-binding model gives $N(0) \propto t^{-1}$, but $\langle I^2 \rangle \propto t^2$, and hence $\lambda \propto t$ [41, 42]. More detailed applications of the tight-binding method have in fact been remarkably successful for transition metals such as Nb, Ta and V [43, 47], and confirm the validity of the electron–phonon mechanism in these materials. For example, we show in fig. 6 the compatibility of λ values for Nb estimated from the transport data [23], and from the

Fig. 6



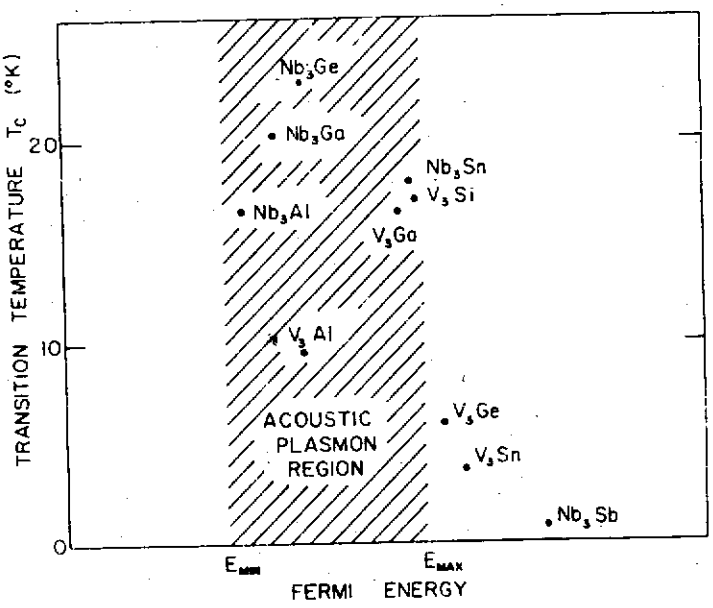
Estimates of the electron–phonon coupling λ for Nb_3Ge and Nb obtained from transport measurements, tight-binding calculations, and the APW method. The dotted line is drawn to indicate the scaling of λ with respect to the bandwidth in the tight-binding theories.

tight-binding calculations [43, 45, 46], spanning the value $\lambda \simeq 0{\cdot}8$ required to give the corrent T_c in the BCS theory. By contrast, corresponding calculations for Nb_3Ge and other A-15 compounds give $\lambda \simeq 0{\cdot}2$ [47, 48], which happens to be close to the estimates from transport data shown in fig. 6. Such small values of λ would give T_c in the milliKelvin range on the basis of the electron–phonon mechanism of superconductivity. Moreover, many measurements (for example, of specific heat) have shown that the density-of-states for the high-T_c materials Nb_3Ge and Nb_3Al are low in comparison with the other A-15 compounds and with transition-metal elements such as Nb.

More detailed theories of the electron–phonon effects have been explored. A phase shift analysis using the APW formalism has been presented in [31] and [49] using as basis the Gaspari–Gyorffy formalism [46]. Sample cases [31] of λ for Nb and Nb_3Ge are shown in fig. 6, and fall considerably above the other estimates. It has been noted [50] that these results are quite sensitive to the choice of boundary conditions, and further investigations are in progress.

Tunnelling spectroscopy has provided the traditional method for determining the role of phonons in superconductivity by identifying structure in the spectrum with independent neutron scattering of the phonon density of states. In metals such as Pb the correspondence between the two measurements is good to within 1%, leaving no doubt regarding the electron–phonon coupling. Again the A-15 compound case poses anomalies in that the

Fig. 7



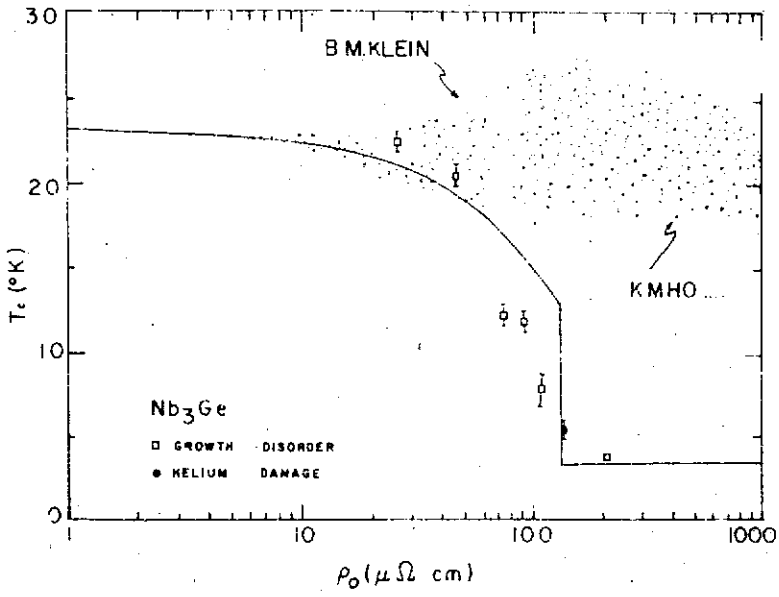
Correlation of the observed superconducting transition temperature with the placement of the Fermi energy relative to the narrow Γ_{12} energy band shown in fig. 2 for Nb_3Ge. Acoustic plasmons should exist in the shaded region according to the model calculations of [22].

tunnelling spectrum differs from the available neutron data, perhaps reflecting a hybridization of the phonons with low-lying phonons [24]. Another explanation may be the poor surface quality of the transition metal tunnel junctions, which are prone to oxidation.

The A-15 compounds thus stand out as candidates for an alternative superconducting mechanism. It is interesting to correlate the expected existence of acoustic plasmons with T_c as shown in fig. 7. The placement of the Fermi energy within the Γ_{12} d-band of fig. 2 is the crucial criterion for acoustic plasmons. From fig. 7 it appears that in fact the known high T_c compound, and also Nb_3Si with $T_c \simeq 18$ K, should exhibit acoustic plasmons, whereas the three low T_c compounds V_3Ge, V_3Sa and Nb_3Sb have filled d-bands preventing the low-lying plasma oscillation.

Indirect evidence for the participation of acoustic plasmons in superconductivity is provided by the anomalous depression of T_c in A-15 compounds by various types of disorder [28, 29]. Unlike most superconductors which are relatively unaffected by disorder, the T_c for Nb_3Ge and other A-15s decreases as the residual resistivity increases, as shown in fig. 8. Previous attempts to explain this in terms of a disorder-induced broadening of a sharp peak in the electron density of states $N(E)$ with a consequent reduction in electron–phonon coupling, λ, are not supported by recent band-structure calculations [30]. For the APW density of states [31] the disorder-induced smearing actually *increases* $N(0)$, as shown in fig. 8. Calculations using pseudopotential techniques [15] allow only a slight change of T_c.

Fig. 8



Superconducting transition temperature of Nb_3Ge subjected to various types of damage. The shaded region indicates changes in T_c compatible with broadening of the electronic density of states. The solid curve shows the theoretical calculation of damped acoustic plasmons whose lifetime is simply related to the residual resistivity.

If the superconductive pairing were due to exchange of acoustic plasmons, damping of the plasmons would provide a simple explanation for the variation of T_c with residual resistivity ρ_0. We may use the standard conductivity formula $\sigma = ne\tau/m$ to write the resistivity

$$\rho = \frac{4\pi}{\omega_{pl}^2}\,\tau^{-1}, \tag{24}$$

to test the overdamped mode criterion

$$\Omega\tau \simeq 1. \tag{25}$$

Since the plasmon frequency $\omega_{pl}(\simeq 2\text{ eV})$ is known from optical data, and the maximal acoustic plasmon frequency in Nb_3Ge is approximately the bandwidth $\Omega \cong t \cong 0{\cdot}2$ eV, we can readily determine that the acoustic plasmons become overdamped for resistivities $\rho_0 \geqslant 100\,\mu\Omega$ cm. This value is close to the sudden drop in T_c shown in fig. 8.

A quantitative study of the transition temperature T_c as a function of disorder requires knowledge of the coupling parameters of the electrons to phonons λ_{ph} and plasmons λ_{pl}, and also the respective 'Debye' energies θ_D for the phonon and θ_{pl} for the plasmon. Regrettably none of these four parameters is known, and their variation with concentration requires by necessity some reasonable speculation. First of all, we presume that the phonon parameters are unaffected by disorder: this seemingly drastic step is certainly consistent with many superconducting materials whose T_c values are insensitive to disorder. Then we pin down the value of $\theta_{pl} \cong 0{\cdot}2\text{ eV} \cong 2000$ K to be consistent with the known bandwidths of the localized electron states near the Fermi energy of Nb_3Ge. Finally then we use a weak coupling formulation [24] of the BCS theory to incorporate both phonon and plasmon exchange contributions to the electron pairing to derive the formula

$$T_c \cong 0{\cdot}7\theta_D \left(\frac{\theta_{pl}}{\theta_D}\right)^{\lambda_{pl}/\lambda_{tot}} \exp\left\{-\frac{1+\lambda_{tot}}{\lambda_{tot}-\mu^*}\right\}, \tag{26}$$

where $\lambda_{tot} = \lambda_{pl} + \lambda_{ph}$. Finally we adjust the electron (plasmon) parameters to yield $T_c = 23$ K by choosing $\lambda_{pl} \cong 0{\cdot}2$. Note that this step presumes that $\lambda_{ph} \simeq 0{\cdot}2$ in keeping with the transport data estimates.

Finally some insight in the T_c variation with disorder is achieved by choosing a linear dispersion for the plasmon $\Omega_{pl} \cong sq$, and deriving the variation in the electron–plasmon coupling $\lambda_{pl}(\tau)$ as a function of damping [30]. Using eqn. (24) we then calculate λ_{pl} and subsequently T_c from eqn. (26) to obtain the curve shown in fig. 8. Despite the crude nature of these approximations, the agreement of the $T_c(\rho_0)$ curve with the data on Nb_3Ge supports the notion that an electronic mechanism is involved in the superconductivity of this class of compounds.

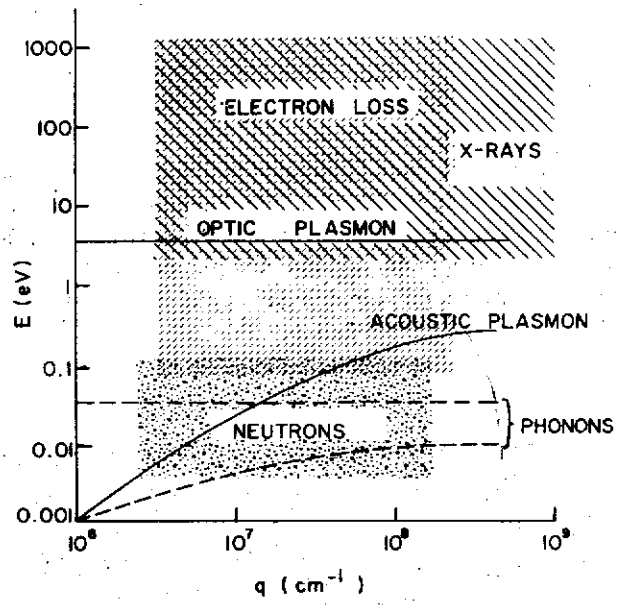
We conclude this section with reference to the challenging problem of determining the magnitude of the electron–plasmon interaction. Although various calculations [16, 18] yield coupling strengths corresponding to $T_c \sim 10^2$ K, other, recent, computations yield much smaller values [52]. These computations were based on the effective mass model at various electron densities and mass ratios m_d/m_s. A more realistic model for the A-15 compounds would be the tight-binding energy bands discussed above, and further

microscopic calculations of the plasmon contribution to T_c would appear to be warranted.

§ 4. Experimental probes

A serious impediment to the study of acoustic plasmons is the lack of any experimental evidence for or against their existence, as well-defined excitations, in any material. This situation is less surprising when note is taken of the fact that their ranges of momentum and energy are not accessible to standard experimental probes, as shown in fig. 9.

Fig. 9



A schematic plot of energy and momentum regions accessible to neutron and X-ray scattering and electron-loss spectroscopy. The acoustic plasmon regime has not yet been investigated by any of these techniques.

Neutron scattering cross-sections fall off rapidly at higher energies, and the neutrons in any event would not couple directly to the plasmons. There is the possibility that hybridization of acoustic plasmons with optical phonons would yield an indirect coupling. In the case of the A-15 compounds, however, electron–phonon couplings are weak and, in any case, there are material obstacles to the growth of large single crystals such as are required for conventional neutron scattering. Neutron spallation sources, with higher fluxes and wider energy spans, may be better suited for this problem.

At first glance, light scattering would seem to be ruled out as a probe by virtue of the long wavelength. However, the metallic nature of the materials yields penetration depths of the light of order 300 Å, and the uncertainty principle, $\Delta x \Delta p \sim \hbar$, suggests that a substantial region of the Brillouin zone would be sampled by the light. Of course the averaging over momentum

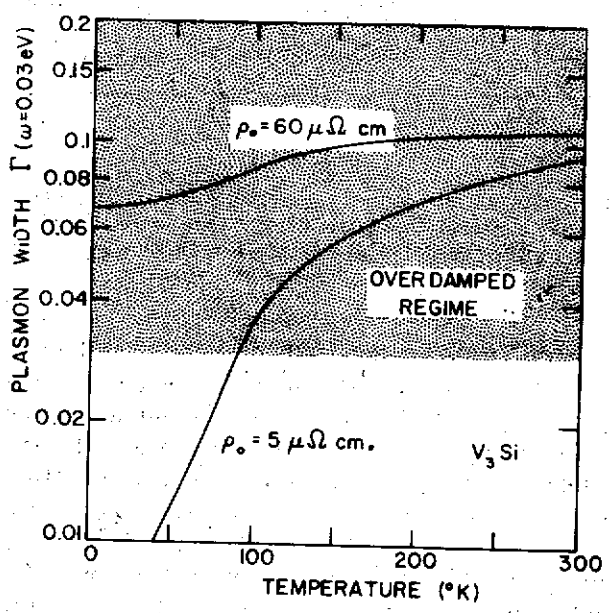
will tend to smear out the Van Hove singularities from the acoustic plasmon dispersion, but nevertheless it may be possible to see structure in the higher energy range $\sim 0{\cdot}2$ eV. To date, the Raman scattering from doped silicon [15] has indicated overdamped low-lying electronic excitations, and the reflectivity studies of the mixed valence compound SmS suggest an additional zero in the dielectric function in the low frequency range [25].

X-ray scattering is a conventional means to study the energy and dispersion of ' optical ' plasmons at $E > 1$ eV. Present techniques have not been applied to the lower energies needed to test for acoustic plasmons.

Electron loss experiments are ideal in the sense that electrons couple strongly to plasmons, and they probe various regions of energy and momentum with fine resolution. Unfortunately, as indicated in fig. 9 the lower limit of this technique falls above the acoustic plasmon regime because of the strong elastic background. If the latter complication could be reduced, by transmission experiments on ultra-thin samples, advanced electron–loss spectroscopy may provide the ultimate test of the width of the plasmon mode as well as its dispersion.

Finally, we remark on the damping problem which plays a recurrent theme in the theoretical developments. As discussed in the various references on the subject, the Landau damping of the *d*-electron plasma by decay into the *s* electron–hole continuum can be minimized to less than 10% of the energy by proper choice of electronic band parameters. However, the

Fig. 10



The acoustic plasmon width in V_3Si is plotted as a function of temperature for two values of the residual resistivity. Because of the strong variation of the resistivity $\rho(T)$ as seen in fig. 5, low temperatures and quite pure samples are required to detect the acoustic plasmon mode.

impurity scattering gives a strong constraint on the plasmon width. We estimate this effect using the resistivity relations (eqn. (24)) for the plasmon width $\Gamma = \tau^{-1}$ for V_3Si. The appropriate plasma frequency of $\omega_{pl} \cong 1{\cdot}6$ eV, may be inserted along with the measured resistivity $\rho(T)$ for samples with disorder characterized by a residual resistivity ρ_0 shown in fig. 10. This result shows vividly that very pure samples of the A-15 compounds similar to V_3Si are required to achieve well-defined acoustic plasmons. Even in the purest cases, the modes become overdamped at room temperature if the measured resistivity is used as a guide to the *d*-electron plasma oscillations. Thus, these experiments require low temperature techniques in conjunction with innovative sample preparation.

§ 5. Conclusions

In summary, the theoretical research on acoustic plasmons remains optimistic, with particular attention being paid to real material in recent years. Semiconductors have received less attention recently. Though doping semiconductors should allow flexibility in choosing values for the electron screening parameters, damping associated with the impurity scattering may prevail. In regard to the possibility that acoustic plasmons may be involved in the superconductivity of A-15 compounds, the correlation between T_c and the appropriateness of the band-structure for the formation of acoustic plasmons is certainly suggestive. Furthermore, the expected damping of plasmons by disorder corresponds quite well with the observed anomalous depression of T_c by radiation damage in Nb_3Ge and other materials. Further work is required on the microscopic calculations of electron–plasmon interactions to settle the upper limits on the transition temperature which may be achieved by the plasmon mechanism.

Other theoretical questions which need to be addressed include the role of dimensionality and surface boundary conditions on the acoustic plasmon dispersion. There are preliminary indications that one-dimensional electronic structures are far more favourable to the existence of these modes, although this advantage is largely offset by the impure nature of the available organic compounds. Surface excitations in systems with two types of electronic carriers are also of interest, and may have a bearing on the experimental prospects of observing analogous modes.

Other interesting properties of solid state plasmas are discussed in the excellent review of Platzman and Wolff [53], which includes analogies to the extensive work on acoustic modes in classical plasmas. The prospects of achieving desirable conditions for many of these effects in semiconductors have unfortunately dimmed recently, as modern data has refined our knowledge of their band structures. Although carriers with disparate masses are commonplace in doped Si and other materials, their relative densities are not sufficient to yield acoustic plasmons. More likely candidates are Bi and Sn based alloys whose electronic structure is sensitive to pressure as well.

Finally, the experimental situation is unusually sparse in view of the theoretical optimism on the existence of acoustic plasmons. In addition to the methods discussed in § 4, acoustic attenuation studies and novel surface techniques are most welcome in the search for these elusive excitations.

Acknowledgments

It is a pleasure to acknowledge discussions with various colleagues, with special thanks to L. M. Kahn, C. Soukoulis and I. Tüttö for their valuable contributions to this work. I am grateful for stimulating comments and suggestings from F. Brosens, M. L. Cohen, J. T. Devreese, W. Kohn, D. Scalapino, S. Schnatterly, J. R. Schrieffer and J. Zak. This research was supported by NSF Grant No. DMR77-13167.

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