Relation between Superconductivity and Lattice Instability in the β-W Compounds

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The temperature T_0, at which the shear modulus $\frac{1}{2}(C_{11}-C_{12})$ vanishes in the cubic phase and in the normal state of some high superconducting β-W compounds, is calculated as a function of the small number Q of electrons (or holes) in the nearly empty (or nearly full) d subband. The variation of T_c with Q was calculated in a previous paper. We show that T_0 is much more sensitive than T_c to the value of Q, and thus to the exact chemical composition of the A_3B phase. Moreover, we show that when Q falls in some range of its value, a linear extrapolation at low temperatures cannot be used to obtain the value of T_0. [In other words, the temperature T_0' at which the extrapolated value of $\frac{1}{2}(C_{11}-C_{12})$ goes to zero may be somewhat different from the temperature T_0 at which $\frac{1}{2}(C_{11}-C_{12})$ is actually zero.] The failure of some samples to undergo the martensitic phase transition, when the extrapolated value of $\frac{1}{2}(C_{11}-C_{12})$ seems to go to zero in the normal state, may be explained in this way. Finally, we find that at room temperature $\frac{1}{2}(C_{11}-C_{12})$ is minimum for some small value of Q.

I. INTRODUCTION

In recent papers[1–4] we have shown that most of the unusual properties of the intermetallic A_3B compounds with the β-W structure could be understood by using a one-dimensional linear-chain model to calculate the d-band structure in the tight-binding approximation. In this model the density of states $n(E)$ has very narrow and high peaks at the d-subband edges. The total number of valence electrons, and thus the Fermi level position E_F, depend on the chemical nature of the elements A and B, and, for a given compound, the exact chemical composition of the A_3B phase. When E_F falls in one of the peaks of $n(E)$, the compound is brought in a strong-coupling limit of the superconductivity.[4] Moreover, large anomalies appear in the temperature variations of the elastic moduli[1,3] and of the Pauli susceptibility.[2] An elastic softening on cooling was observed[5,6] for the shear modulus $\frac{1}{2}(C_{11}-C_{12})$ by measuring the sound velocity of the ultrasonic mode $\langle 110\rangle\{1\bar{1}0\}$. The velocity for this mode is proportional to $(C_{11}-C_{12})^{1/2}$. In some extreme cases, such as V_3Si and Nb_3Sn, the decrease of $C_{11}-C_{12}$ on cooling is so large that the associated increase in the attenuation forbids the propagation of the $\langle 110\rangle\{1\bar{1}0\}$ mode in the limit of low temperatures. In those cases, by linearly extrapolating the measured variations of $C_{11}-C_{12}$ at low temperatures, it is found that this parameter would go to zero at a low but nonzero temperature T_0'. If $C_{11}-C_{12}$ actually vanishes, the cubic phase becomes instable. And in fact, a martensitic phase transformation was observed in several samples of V_3Si and Nb_3Sn, resulting from the elastic softening on cooling.[5,7,8] In the samples where this transformation takes place, it does at a temperature T_m not much larger than T_0'. All the experimental evidence indicates that T_0' and T_m are much more sensitive than the superconducting critical temperature T_c to the exact chemical composition of the A_3B phase, for a given compound. Variations of T_0' and T_m of several degrees are observed among samples, all of them with the same T_c. In some samples, the martensitic phase transformation does not occur. In this paper we calculate the temperature T_0 at which $C_{11}-C_{12}$ actually is zero in our model, in the normal state and in the cubic phase. We find that in some cases T_0 may be different from the temperature T_0' at which the linearly extrapolated calculated value of $C_{11}-C_{12}$ goes to zero. We show how the temperature T_0 and T_c are related, as resulting from the comparison of their calculated variations versus the small number Q of electrons (or holes) in the nearly empty (or nearly full) d subband responsible for the anomalous properties. We shall neglect in this paper the difference between T_0 and T_m, which is generally small. This allows us to restrict the discussion to the cubic phase. (For a strictly second-order phase transition we should have $T_m=T_0$. In fact, in our model the transition is a first-order one. But the calculated discontinuities of the parameters and the calculated latent heat are small.)

II. CALCULATION OF TEMPERATURE T_0

We shall first give the results of our calculations concerning the influence of Q on the variations of $M=$

* This work will be included in a thesis to be submitted by J. Labbé in 1968 to the Faculté des Sciences d'Orsay, in partial fulfillments of the requirements for the Doctorat d'État ès Sciences Physiques.

[1] J. Labbé and J. Friedel, J. Phys. (Paris) **27**, 153 (1966); **27**, 303 (1966); **27**, 708 (1966).

[2] A. C. Gossard, Phys. Rev. **149**, 246 (1966); J. Labbé, *ibid.* **158**, 647 (1967); **158**, 655 (1967).

[3] S. Barisic and J. Labbé, J. Phys. Chem. Solids **28**, 2477 (1967).

[4] J. Labbé, S. Barisic, and J. Friedel, Phys. Rev. Letters **19**, 1039 (1967).

[5] L. R. Testardi and T. B. Bateman, Phys. Rev. **154**, 402 (1967).

[6] K. R. Keller and J. J. Hanak, Phys. Rev. **154**, 628 (1967).

[7] R. Mailfert, B. W. Batterman, and J. J. Hanak, Phys. Letters **24**, 315 (1967).

[8] B. W. Batterman and C. S. Barrett, Phys. Rev. **145**, 296 (1966).

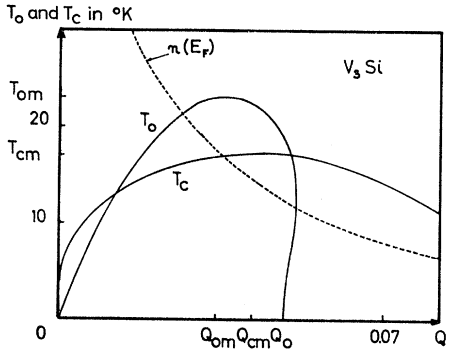

FIG. 1. Variations of T_0 and T_c versus the small number Q of electrons in the d subband in V_3Si.

$\frac{1}{2}(C_{11}-C_{12})$ versus the temperature T. In a previous paper[1] we had shown that in the cubic phase

$$M=\tfrac{1}{6}a^2q^2\left\{\int_{E_m} EnfdE+\int_{E_m} E^2nf'dE\right\}+M', \quad (1)$$

where a is the interatomic distance in a linear chain of transition atoms, q is the Slater coefficient for the atomic d orbitals, E is the energy of one electron, E_m is the bottom of the d subband under consideration, n is the density of states for this d subband, f is the Fermi distribution function and f' its derivative versus E, and M' is the temperature-independent contribution from the lattice, including the s-electron conduction band and the other d subbands. The electronic transfer between the different bands can be neglected in the calculation of the shear modulus, as shown by Barisic.[3] Thus the change of Fermi level E_F is obtained by writing Q as a constant:

$$\int_{E_m} nfdE=Q. \quad (2)$$

When E_F is not too far from the edge E_m of the d subband we may use for the density of states the simplified form $n\simeq(Z/\pi w^{1/2})(E-E_m)^{-1/2}$, where Z is the number of available states in the d subband for the two spin directions, and w is the subband width. Equations (1) and (2) give

$$M=M'+(Z^2a^2q^2w/6\pi^2Q)(S-R)R, \quad (3)$$

$$k_BT=(\pi^2wQ^2/4Z^2)R^{-2}; \quad (4)$$

k_B is the Boltzmann constant and we have introduced the functions R and S of the parameter $\eta=(E_F-E_m)(k_BT)^{-1}$ defined by

$$R=\int_0^\infty [1+\exp(x^2-\eta)]^{-1}dx,$$

$$S=\int_0^\infty [1+\exp(x^2-\eta)]^{-2}dx.$$

By tabulating R and S, we obtain the variations of M versus T. Here we defined T_0 as the temperature for which $M=0$. But it must be kept in mind that T_0 may be somewhat different from the value T_0' of the temperature for which the linearly extrapolated variation of M at low temperature goes to zero. In fact, we shall see that when Q falls in some range of values, M stops decreasing linearly with T in the cubic phase just before going to zero. (This phenomenon, which takes place in the cubic phase, must not be confused with the arrest of the linear decrease of M at the martensitic phase transition temperature T_m.) Now we calculate T_0 by solving Eqs. (3) and (4) for $M=0$. Its variations versus Q are shown in Fig. 1 for V_3Si and in Fig. 2 for Nb_3Sn, where the variations of T_c calculated in a previous paper[4] have also been plotted for comparison, and where we have roughly indicated the behavior of the density of states at Fermi level, which is the monotically decreasing function of Q given by $n(E_F)\simeq 2Z^2/\pi^2wQ$. The curves of Figs. 1 and 2 have been obtained using parameters which are determined in the last part of this paper. The following results may be given:

(a) Except in the neighborhood of $Q=0$, T_0 varies more rapidly than T_c with Q.

(b) T_0 vanishes for $Q=0$ and for a small value $Q_0=(Z^2/12\pi^2)a^2q^2(w/M')$ of Q. We shall see in Sec. III that, as a typical order of magnitude, Q_0 should fall in the range from 10^{-2} to 10^{-1} electrons in the d subband per transition atom.

(c) T_0 is maximum for $Q_{0m}=0.715Q_0$, with the value

$$T_{0m}=0.0011(Z^2/\pi^2)a^4q^4(w^3/k_BM'^2). \quad (5)$$

T_c is maximum for $Q_{cm}=1.9(Z^2/\pi^2)V/w$, with the value $T_{cm}=0.51(Z^2/\pi^2)V^2/k_Bw$, where V is the BCS coupling constant, as shown in our paper.[4] The ratio

$$T_{0m}/T_{cm}=2.1(Q_{0m}/Q_{cm})^2=0.0021(a^4q^4w^4/V^2M'^2) \quad (6)$$

very strongly depends on the parameters.

(d) At the origin $Q=0$, T_0 starts to increase linearly with Q, while T_c starts to increase as $[\ln(1/Q)]^{-1}$,

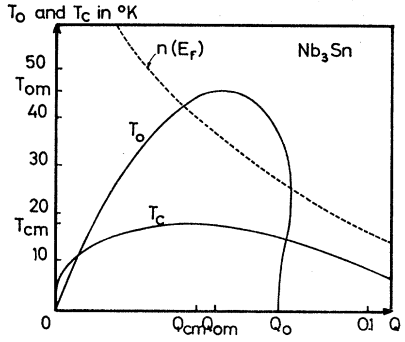

FIG. 2. Variations of T_0 and T_c versus the small number Q of electrons in the d subband in Nb_3Sn.

with an infinite slope at $Q=0$. For $Q \ll Q_0$ the following holds:

$$T_0/T_{0m}=3.2Q/Q_0-1.8(Q/Q_0)^{3/2}+O(Q/Q_0)^2. \quad (7)$$

(e) For $Q>Q_{0m}$ the decrease of T_0 from its maximum value T_{0m} to zero is very sharp, and for $Q>1.057Q_0$, $C_{11}-C_{12}$ no longer goes to zero at low temperature. In the very narrow range $Q_0<Q<1.057Q_0$, the curve which gives T_0 versus Q has two branches (the lowest one is related to the existence of metastable states in the cubic phase). Contrary to T_0, the decrease of T_c for $Q>Q_c$ is very slow.

Equation (6) shows that for reasonable numerical values of the parameters ($aq\simeq 1$, $w\simeq 8$ eV, $M'\simeq 10$ eV atom^{-1}, $V\simeq 0.15$ eV) Q_{0m} cannot be much larger than Q_{cm}, which is itself small (probably not larger than 10^{-1} electron/atom in the d subband). Thus the shear modulus M can go to zero at low temperature only when Q is small enough to bring the compound in the strong limit of the superconductivity defined in our previous paper.[4] And we may conclude that the martensitic phase transition can take place only in those β-W compounds which have a high critical superconducting temperature T_c.

But conversely, the sharp decrease of T_0 for $Q>Q_{0m}$, compared with the slow decrease of T_c for $Q>Q_{cm}$, shows that a large value of T_c is not necessarily associated with a decrease of M large enough to trigger the martensitic phase transition. For Q a little larger than Q_0 (Figs. 1 and 2), M no longer goes to zero, but T_c may be large again. This should explain why the martensitic phase transition was observed only in some of the high superconducting β-W compounds. So far, it was observed only in V_3Si and Nb_3Sn.

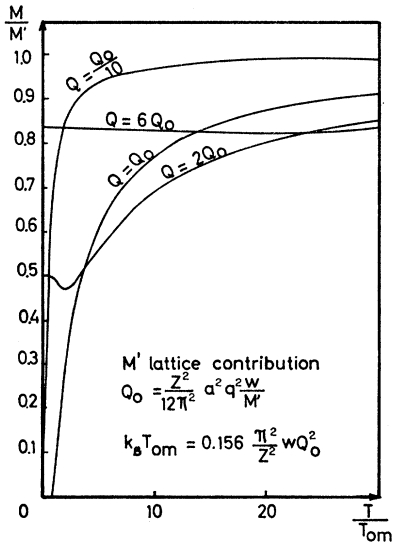

FIG. 3. Variations of the shear modulus $M=\frac{1}{2}(C_{11}-C_{12})$ versus the temperature T, for different values of Q.

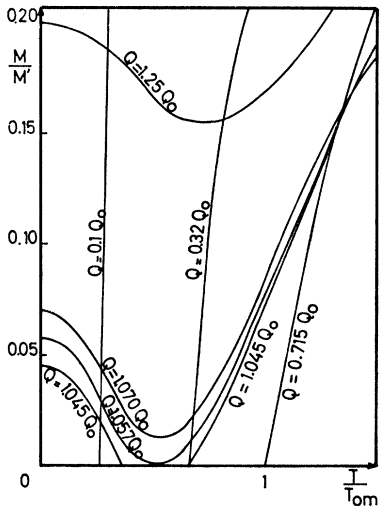

FIG. 4. Variations of the shear modulus $M=\frac{1}{2}(C_{11}-C_{12})$ versus the temperature T for the small values of Q.

On the other hand, for a given β-W compound, where Q falls in the neighborhood of Q_0, we may assume that a small change in the chemical composition, at the departure from the stoichiometry, may produce a change in Q able to make the lattice instability appear or disappear, without any large change in the value of T_c. This should explain why, even in V_3Si and Nb_3Sn, the martensitic phase transformation was not observed in all the samples.[5–8] And in those samples where it was observed, the variations of T_0 from one sample to another may be also understood as caused by small changes in Q.

III. RESULTS FOR THE SHEAR MODULUS $M=\frac{1}{2}(C_{11}-C_{12})$

By using M/M', T/T_{0m}, and Q/Q_0 as dimensionless parameters, we have plotted in Figs. 3 and 4 the variations of M/M' versus T/T_{0m} for different values of Q/Q_0, as calculated from Eqs. (3) and (4). We see in Fig. 3 that the lattice instability exists only when Q is small. And we see in Fig. 4 that when Q is in the neighborhood of Q_0, small variations of its value are sufficient to produce a significant change in the thermal variation of M at low temperature. It is interesting to compare the results shown in Fig. 4 with the experimental data of Testardi and Bateman[5] for different samples of V_3Si.

In fact, it appears that a linear extrapolation to low temperatures of the measured thermal variation of M can predict that M goes to zero at a finite temperature, when actually it does not. This can occur when Q is just in the neighborhood of $1.057Q_0$ or a little larger than this value. For instance, the curve with $Q=1.070Q_0$ in Fig. 4 stops decreasing linearly just a little before that M for which it can go to zero, and in fact

M does not vanish for this value of Q. This could be one of the possible reasons why the martensitic phase transition was not observed in samples of V_3Si or Nb_3Sn in which M *seemed* to vanish by extrapolation.[6] In these samples, the actual value of M in the cubic phase may in fact not completely go to zero, even in the normal state.

On the other hand, Testardi and Bateman have observed in a sample of V_3Si an arrest of the decrease of M just at the onset of the superconductivity at $T_c \simeq 17°K$. This phenomenon may be at least qualitatively understood in our model by the fact that for $T<T_c$ the electronic distribution is no longer determined by the Fermi function, the width of which goes to zero with T, but by the function $g_k=(1-v_k^2)f_k+v_k^2(1-f_k)$, which keeps a finite and slowly varying width from T_c to the absolute zero,[4] where $2v_k^2=1-\xi_k/\epsilon_k$, $f_k^{-1}=1+\exp(\epsilon_k/k_BT)$, with $\xi_k=E(k)-E_F$ and $\epsilon_k=(\xi_k^2+\Delta^2)^{1/2}$. So, if the cubic phase is stable at T_c, it should usually keep its stability for $T<T_c$. It may be for the same reason that in the transforming samples the lattice distortion seems to stop increasing on cooling just when T becomes smaller than T_c, as observed in V_3Si by Batterman and Barrett.[8] But, of course, the onset of the superconductivity, at $T_c \simeq 18°K$, cannot explain why no martensitic phase transition was detected in a sample of Nb_3Sn where the extrapolated value of M should have gone to zero at $T_0' \simeq 32°K$, and thus in the normal state.[6] (The phase transition takes place in the same sample after an appropriate metallurgical treatment has made it more stoichiometric.[7])

A third possible reason of the failure of the nonstoichiometric compounds to transform may be due to the martensitic nature of the phase transition. The involved mechanism needs the migration throughout the crystal of an interface which produces a twinned tetragonal structure by a double shear. The departure from the stoichiometry is obviously associated with small irregularities in the lattice arrangement, such as excess of atoms of one kind at wrong sites. These irregularities may, by a mechanism which in fact is not well known, quench the migration of any interface, and thus forbid the transition.

Another interesting phenomena appears by plotting the variations of M/M' versus Q/Q_0 for different values of T/T_{0m}, as shown in Fig. 5. We see that for a given value of T (for instance room temperature) the shear modulus M is minimum for a small value of Q which does not vary very much with T and falls in the range from 0.7 to $3Q_0$. This should be compared with the recent observation by Matthias[9] of the existence of a minimum of M at the room temperature in the ternary phase diagram formed by Nb_3Sn, Nb_3Al, and Nb_3Ge near the composition 4 Nb_3Al:1 Nb_3Ge.

[9] B. T. Matthias, Phys. Letters **25**, 226 (1967).

Finally, we shall give the asymptotic expansions of the shear modulus M in the two extreme cases of the very small and the large values of Q. For $Q/Q_0 \ll T/T_{0m}$ we find

$$M/M' \simeq 1-3.20(T_{0m}/T)Q/Q_0+3.23(T_{0m}/T)^{3/2}(Q/Q_0)^2. \quad (8)$$

For $Q \gg Q_0$ (but with $Z \gg Q$) we find the temperature-independent limit $M/M' \simeq 1-Q_0/Q$.

IV. NUMERICAL RESULTS IN Nb_3Sn AND V_3Si

A. Nb_3Sn

The highest value at which the martensitic phase transition was observed in Nb_3Sn is 43°K.[7] It seems reasonable to assume that T_{0m} is not much larger than this value, which thus should correspond to a value of Q not very different from $Q_{0m} \simeq 0.715Q_0$. But in Nb_3Sn the measured distorsion ϵ_m^- is negative[7] ($\epsilon_m^- \simeq -0.0041$), so we conclude from our first paper[1] that $Q<\frac{2}{3}Q_0$. Finally, to satisfy the two previous conditions, we shall assume that Q falls in the neighborhood of $0.6Q_0$. At room temperature $T=300°K \simeq 7T_{0m}$, and with $Q=0.6Q_0$, Eq. (8) gives $M \simeq 0.8M'$. But at this temperature the experimental data[6] are $M=10.9$ eV/niobium atom. Therefore we obtain $M' \simeq 13.6$ eV/niobium atom.

The formula $\epsilon_m^- \simeq -aqwQ/6M'$ (formula I, 32 of our first paper) gives $aqwQ \simeq 0.336$. We shall use the result of Morin and Maita[10] for the density of states at Fermi level in the cubic phase $n(E_F) \simeq 2Z^2/\pi^2wQ \simeq 8.8$ states eV^{-1}/niobium atom and for the two spin directions. With $Z=4(d_{x^2-y^2}d_{xy}$ subband, for instance) we find $wQ \simeq 0.37$ and thus $aq \simeq 0.91$, $q \simeq 0.34$ Å^{-1}, $w \simeq 8.7$ eV, and $Q_0 \simeq 0.071$ electron/niobium atom in the subband. Equation (5) gives $T_{0m} \simeq 45°K$. Finally, we know that in Nb_3Sn, T_c was never observed to be much larger than 18°K. (The larger value $T_c \simeq 20°K$ was discovered by Matthias[11] in the ternary compound 4 Nb_3Al:1 Nb_3Ge. But we do not know precisely the

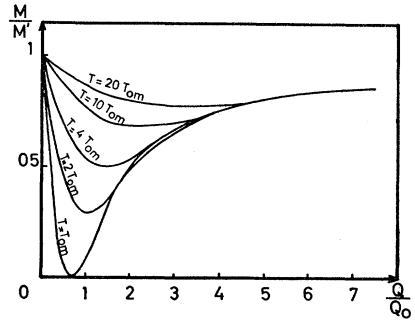

FIG. 5. Variations of the shear modulus $M=\frac{1}{2}(C_{11}-C_{12})$ versus the number Q of electrons in the d subband, for different values of the temperature T.

[10] F. J. Morin and J. P. Maita, Phys. Rev. **129**, 1115 (1963).
[11] B. T. Matthias, Science **156**, 645 (1967).

parameters of this compound.) By assuming $T_{cm}\simeq 18.5°K$, we find $V\simeq 0.13$ eV and thus $Q_{cm}\simeq 0.88Q_{0m}\simeq 0.63Q_0$ as shown in Fig. 2.

B. V_3Si

The highest value observed for T_m in V_3Si does not exceed 25°K.[8] The measured distorsion $\epsilon_m{}^+$ is positive ($\epsilon_m{}^+\simeq 0.00167$). So we assume that $Q\simeq 0.75Q_0$ for a typical sample. Numerical estimations very similar to those for Nb_3Sn, but with $\epsilon_m{}^+=aqwQ/12M'$ (formula I, 21 of Ref. 1), give $M'\simeq 10.5$ eV/vanadium atom, $aq\simeq 0.65$, $q\simeq 0.28$ Å^{-1}, $w\simeq 8.9$ eV, $Q_0\simeq 0.048$ electron/vanadium atom in the subband, $T_{0m}\simeq 23°K$, $V\simeq 0.13$ eV, and $Q_{cm}\simeq 1.25Q_{0m}\simeq 0.89Q_0$, as shown in Fig. 1.

We see that the estimated parameters M', aq, w, and V have the same order of magnitude in Nb_3Sn and V_3Si, as it is reasonable to expect. The large difference in the value of T_{0m} for these two compounds is due to the fact that the parameters enter in the formula (5) with high powers. The *absolute* number Q of electrons per transition atom in the subband is smaller in V_3Si than in Nb_3Sn (we find $Q\simeq 0.036$ in V_3Si and 0.043 in Nb_3Sn). But the *relative* number Q/Q_0 is larger in V_3Si, in agreement with the sign of the distortion.

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High-Frequency Sound Absorption in Superconductors*

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Theoretical and numerical results for the attenuation of high-frequency sound waves in superconductors are presented. Explicit calculations are given for the attenuation of longitudinal sound waves with wavelengths both large and small compared with the electron mean free path in pure superconductors and in superconductors containing magnetic impurities. Extensions to more general situations are discussed. The contribution due to the disruption of Cooper pairs by phonons is examined as a function of impurity concentration.

I. INTRODUCTION

MEASUREMENTS of the attenuation of high-frequency sound have provided a useful and relatively direct means of studying the magnitude and anisotropy of the temperature-dependent energy gap in superconductors, as well as providing one of the many verifications of the validity of the presently accepted theory.[1] The theoretical description appropriate to such measurements was developed in the original work of Bardeen, Cooper, and Schrieffer[2] in an intrinsically low-frequency calculation. They found the remarkably simple result that the ratio of the attenuation in the superconductor to that in the normal metal should be given by

$$\alpha_s/\alpha_n=2f(w_g), \tag{1}$$

where $f(w_g)$ is the Fermi function

$$1/\{1+\exp[w_g(T)/kT]\},$$

and $2\omega_g(T)$ is the temperature-dependent energy gap parameter. The only contribution included here is that due to scattering of phonons from thermally excited quasiparticles. Although originally derived for longitudinal waves in the limit $ql\gg 1$, where q is the wave vector of the sound and l is the electronic mean free path, (1) has since been found to hold for arbitrary mean free paths (for longitudinal waves) and for the residual low-frequency attenuation of transverse waves[3]

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[1] Some examples of recent measurements are J. M. Perz and E. R. Dobbs, Proc. Roy. Soc. (London) **A296**, 113 (1967); J. R. Liebowitz, Phys. Rev. **133**, A84 (1964); A. C. E. Sinclair, Proc. Phys. Soc. (London) **97**, 962 (1967). A summary of such measurements may be found in L. M. Falicov and D. H. Douglass, in *Progress in Low Temperature Physics*, edited by J. C. Gorter (North-Holland Publishing Co., Amsterdam, 1964), Vol. 4, pp. 97–189.

[2] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957), hereafter referred to as BCS.

[3] T. Tsuneto, Phys. Rev. **121**, 402 (1961). Recent thorough discussions of the low-frequency theory for pure superconductors are given by L. P. Kadanoff and A. B. Pippard, Proc. Roy. Soc. (London) **A292**, 299 (1966); J. M. Perz, Can. J. Phys. **44**, 1765 (1922).