PHYSICAL REVIEW VOLUME 137, NUMBER 5A 1 MARCH 1965

Electron Contribution to the Temperature Dependence of the Elastic Constants of Cubic Metals. II. Superconducting Metals

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(Received 15 October 1964)

A theory is presented to explain the difference in elastic shear constants between normal and superconducting metals as a function of temperature. The development is based upon the BCS theory of superconductivity in the weak-coupling limit and the quantum mechanical theory of elasticity discussed in the first article of this series. Expressions are presented for the first and second derivatives of the energy gap and critical field with respect to shear strains in terms of parameters for the normal state. Representative calculations are performed to show that the model chosen is capable of giving the correct order of magnitude and sign for the difference in elastic shear constants at absolute zero. It is also found that although the second derivative of the free-energy difference, with respect to shear strains, disappears at the superconducting critical temperature, the corresponding second derivative of the entropy difference is finite at the superconducting critical temperature and is proportional to the difference in elastic shear constants at absolute zero.

1. INTRODUCTION

In the preceding article of this work,[1] it was shown that the electrons in a normal metal contribute a term in T^2 to the temperature dependence of the elastic constants at low temperatures. This term in T^2 arises from the temperature dependence of the electron energies and distributions due to the Fermi-Dirac distribution function. The temperature dependence of the elastic shear constants due to the electrons was shown to be directly related to the second derivative of the total density of states at the Fermi level with respect to strain. The magnitude and algebraic sign of the temperature dependence were then shown to depend on the energies of symmetry points in the Brillouin zone and the first and second derivatives of the electron density distribution with respect to energy. On the basis of semiquantitative calculations, it was concluded that the effect is most pronounced for transition elements, exhibiting a high density of states at the Fermi level, in agreement with experiment.[2,3]

Since the elastic constants are second derivatives of the thermodynamic free energy with respect to strain, it is to be expected that the free energy difference between the normal and superconducting states will be reflected by a difference in the elastic constants. Such differences have been experimentally observed by Alers and Waldorf[2] for vanadium and niobium. It is the purpose of this article to examine the effect of the superconducting transition upon the electron contribution to the elastic shear constants, with respect to the theory of superconductivity proposed by Bardeen, Cooper, and Schrieffer.[4] As a result of these calculations, such parameters as the strain dependence of the critical field and critical temperature of a superconductor are obtainable.

[1] B. T. Bernstein, Phys. Rev. **132**, 50 (1963).
[2] G. A. Alers and D. L. Waldorf, Phys. Rev. Letters **6**, 677 (1961).
[3] G. A. Alers (private communication).
[4] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

The elastic constants of metals may be obtained by a direct calculation of the total energy as a function of strain. The total energy of a normal metal is expressed as a sum of separate terms and by calculation of how these terms change as the metal is strained, one can obtain the elastic constants as a sum of separate contributions.[5–8] The theory of superconductivity developed by Bardeen, Cooper, and Schrieffer,[4] referred to as the BCS theory, enables one to obtain the difference in total energy between the normal and superconducting states from absolute zero to the superconducting critical temperature. This energy difference, known as the condensation energy, is used in this work to obtain the difference between the elastic shear constants in the normal and superconducting states.

In Sec. 2 the condensation energy is differentiated with respect to shear strains and it is shown that the difference in elastic shear constants may be represented by the square of the first derivatives of the energy gap with respect to strain. The results of Sec. 2 are used in Sec. 3 to evaluate the change of condensation energy as a function of shear strain for vanadium and niobium. Finally, in Sec. 4 the results of the calculations are summarized and discussed.

2. STRAIN DEPENDENCE OF THE CONDENSATION ENERGY

A. Absolute Zero

The energy difference, $\Delta W(0)$, between the normal and superconducting states at absolute zero is obtained from the BCS theory as

$$\Delta W(0)=W_n(0)-W_s(0)=\tfrac{1}{2}n_c\Delta(0)\,, \qquad (1)$$

where $W_n(0)$ and $W_s(0)$ are the total energies per unit volume in the normal and superconducting states at absolute zero, respectively, n_c is the number of electrons

[5] K. Fuchs, Proc. Roy. Soc. (London) **A153**, 622 (1936).
[6] R. S. Leigh, Phil. Mag. 42, 139 (1951).
[7] J. R. Reitz and C. S. Smith, Phys. Rev. **104**, 1253 (1956).
[8] B. T. Bernstein, J. Appl. Phys. **33**, 142 (1962).

in pairs, per unit volume, virtually excited above the Fermi surface at absolute zero and $\Delta(0)$ is the superconducting energy gap at absolute zero. Since the superconducting energy gap is actually anisotropic, and since the number of electrons virtually excited above the Fermi surface is the sum of separate contributions from electron overlap between symmetry points of the Brillouin zone and the Fermi surface, Eq. (1) can be written as

$$\Delta W(0)=\sum_i \Delta W_i(0)=\sum_i \tfrac{1}{2}n_{c_i}\Delta_i(0). \tag{2}$$

We define here the elastic shear constants as those elastic constants which relate to homogeneous strain without change of volume. For cubic metals we consider the two elastic shear constants[1]

$$C=C_{44} \quad \text{and} \quad C'=\tfrac{1}{2}(C_{11}-C_{12}).$$

If we let $\Delta M(0)$ represent either $\Delta C(0)$ or $\Delta C'(0)$ and X an arbitrary strain parameter, corresponding to η for C and ξ for C' (see Ref. 1), we obtain

$$\Delta M(0)=K\sum_i\left(\frac{d^2\Delta W_i(0)}{dX^2}\right)_0, \tag{3}$$

where the subscript zero indicates the derivative is evaluated at zero strain and the constant K is $\frac{1}{3}$ when $X=\eta$ and $\frac{3}{4}$ when $X=\xi$.

We now make the assumption,[6] that during shear the energy surfaces at each overlap or hole symmetry point in the Brillouin zone move rigidly with the Brillouin zone boundary and that the electron and hole effective masses are not functions of strain. We define by N_i the contribution to the total density of states at the Fermi level, ζ_0, from those electron overlap or hole states with energy at the origin of the overlap or hole of E_i, where i refers to the symmetry point of the zone. We now assume that the total number of overlap electrons below the Fermi surface minus the total number of holes is a constant independent of the state of shear of the crystal. In effect, we are assuming that shear strain does not excite electrons across the superconducting energy gap but redistributes them in phase space above and below the Fermi surface.

The number of electrons excited above the Fermi surface is given by

$$n_{c_i}=\int_0^{\Delta_i} N_i(\omega_i)d\omega_i, \tag{4}$$

where $\omega_i=\epsilon_i-\zeta_0$. Since the superconducting energy gap is of the order of thousandths of an eV, we expand the density of states in a Taylor's series about $\omega_i=0$ by the relation

$$N_i(\omega)=N_i(0)+\omega_i\left(\frac{dN_i}{d\omega}\right)_{\omega=0}+\tfrac{1}{2}\omega_i^2\left(\frac{d^2N_i}{d\omega^2}\right)_{\omega=0}+\cdots \tag{5}$$

to obtain to first order

$$n_{c_i}=\Delta_i\left(N_i(0)+\tfrac{1}{2}\Delta_i\left(\frac{dN_i}{d\omega}\right)_{\omega=0}\right). \tag{6}$$

Differentiation of Eq. (4), with respect to X gives the relation

$$\left(\frac{dn_{c_i}}{dX}\right)_0=N_i(\Delta_i)\left(\frac{d\Delta_i}{dX}\right)_0 =\left(\frac{d\Delta_i}{dX}\right)_0\left(N_i(0)+\Delta_i\left(\frac{dN_i}{d\omega}\right)_{\omega=0}\right). \tag{7}$$

Retaining only the first term in parenthesis in Eqs. (6) and (7), and using the relation

$$\Delta W_i=\tfrac{1}{2}n_{c_i}\Delta_i, \tag{8}$$

we obtain

$$\left(\frac{d\Delta W_i}{dX}\right)_0=n_{c_i}\left(\frac{d\Delta_i}{dX}\right)_0, \tag{9}$$

and

$$\left(\frac{d^2\Delta W_i}{dX^2}\right)_0=N_i\left(\frac{d\Delta_i}{dX}\right)_0^2+\tfrac{1}{2}n_{c_i}\left(\frac{d^2\Delta_i}{dX^2}\right)_0+\tfrac{1}{2}\Delta_i\left(\frac{d^2n_i}{dX^2}\right)_0. \tag{10}$$

Thus Eq. (3) becomes, to first order

$$\Delta M(0)=K\sum_i N_i\left(\frac{d\Delta_i}{dX}\right)_0^2+\tfrac{1}{2}n_{c_i}\left(\frac{d^2\Delta_i}{dX^2}\right)_0, \tag{11}$$

where we have used the assumption that

$$\sum_i\left(\frac{dn_{c_i}}{dX}\right)=\sum_i\left(\frac{d^2n_{c_i}}{dX^2}\right)=0. \tag{12}$$

In addition, we have from Eqs. (9) and (12),

$$\sum_i\left(\frac{d\Delta W_i}{dX}\right)_0=0, \tag{13}$$

which satisfies the equilibrium condition for shear strains.[7] It now remains to evaluate the derivatives of the energy gap as a function of strain in order to evaluate Eq. (11).

The excitation of electrons above the Fermi level in the superconducting state causes the number of overlap electrons and holes and the Fermi level itself to be different from the values in the normal state at absolute zero. Thus, we may write

$$n_{c_i}=\int_0^{\zeta_0^n-E_i}N_i(\omega')d\omega'-\int_0^{\zeta_0^s-E_i}N_i(\omega')d\omega', \tag{14}$$

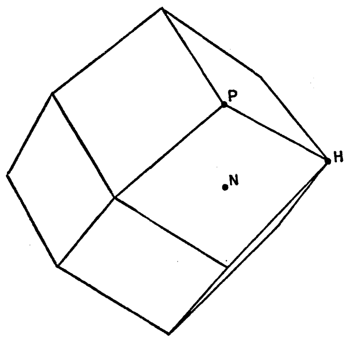

FIG. 1. Brillouin zone for the body-centered cubic lattice with points of symmetry shown.

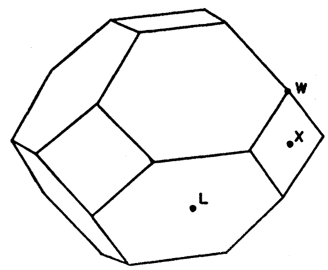

FIG. 2. Brillouin zone for the face-centered cubic lattice with points of symmetry shown.

where $\omega'=\epsilon-E_i$, and ζ_0^n, and ζ_0^s are the respective Fermi levels in the normal and superconducting states at absolute zero. In Eq. (14) we have assumed that the E_i are unaffected by the superconducting transition. Differentiating Eq. (14) with respect to strain gives the result that

$$dn_{c_i}/dX=N_i(\zeta_0^n-E_i)[d(\zeta_0^n-E_i)/(dX)]_0 - N_i(\zeta_0^s-E_i)[d(\zeta_0^s-E_i)/(dX)]_0. \quad (15)$$

As shown in the preceding work[1]

$$(d\zeta_0/dX)_0=0. \quad (16)$$

As a consequence of Eq. (16),

$$(dn_{c_i}/dX)_0=[N_i(\zeta_0^s-E_i) - N_i(\zeta_0^n-E_i)](dE_i/dX)_0. \quad (17)$$

Performing a Taylor's series expansion once again about ζ_0^n, we obtain

$$(dn_{c_i}/dX)_0=-\Delta_i(dN_i/d\omega')_{\omega'=\zeta_0^n-E_i}(dE_i/dX)_0. \quad (18)$$

Thus,

$$N_i(d\Delta_i/dX)_0^2=(\Delta_i^2/N_i)(dN_i/d\omega')^2(dE_i/dX)_0^2. \quad (19)$$

From Eq. (12) we obtain

$$\sum_i N_i\left(\frac{d^2\Delta_i}{dX^2}\right)+\left(\frac{dN_i}{d\omega}\right)_{\omega=0}\left(\frac{d\Delta_i}{dX}\right)^2=0. \quad (20)$$

Now, since the individual $(d\Delta_i/dX)_0^2$ are not necessarily zero and neither is their sum zero, we obtain from Eq. (19)

$$\sum_i N_i\left(\frac{d^2\Delta_i}{dX^2}\right)_0=-\sum_i \frac{\Delta_i^2}{N_i^2}\left(\frac{dN_i}{d\omega}\right)^3\left(\frac{dE_i}{dX}\right)_0^2. \quad (21)$$

Finally, we obtain for $\Delta M(0)$, to first order

$$\Delta M(0)=K\sum_i \frac{\Delta_i^2}{N_i}\left(\frac{dN_i}{d\omega}\right)^2\left(\frac{dE_i}{dX}\right)_0^2 \times\left[1-\frac{1}{2}\frac{\Delta_i}{N_i}\left(\frac{dN_i}{d\omega}\right)\right]. \quad (22)$$

The shear strain dependence of the superconducting critical field at absolute zero is obtained from the relation $H_0^2/8\pi=\Delta W(0)$ as

$$\left(\frac{d^2H_0}{dX^2}\right)_0=\frac{2(2\pi)^{1/2}}{\sum_i(n_{c_i}\Delta_i)^{1/2}}\sum_i\frac{\Delta_i^2}{N_i} \times\left(\frac{dN_i}{d\omega}\right)^2\left(\frac{dE_i}{dX}\right)^2\left[1-\frac{1}{2}\frac{\Delta_i}{N_i}\left(\frac{dN_i}{d\omega}\right)\right]. \quad (23)$$

The Brillouin zones for the body-centered-cubic and face-centered-cubic lattices with points of symmetry designated are shown in Figs. 1 and 2, respectively. In order to simplify the discussion we will assume, as in the preceding work,[1] that the first and second derivatives of the E_i are proportional to E_i, the constant of proportionality being determined by the geometry of the Brillouin zone. The values[1] of K in Eq. (22) are $\frac{1}{3}$ for ΔC and $\frac{3}{4}$ for $\Delta C'$. Assuming an average value for the Δ_i, and referring to Fig. 1, we have for the body-centered cubic lattice

$$\Delta C(0)=\frac{1}{2}\frac{\Delta^2}{N(\zeta_0-E_N)}\left(\frac{dN}{d\omega}\right)^2_{\omega=\zeta_0-E_N}E_N^2\left[1-\frac{1}{2}\frac{\Delta}{N(\zeta_0-E_N)}\left(\frac{dN}{d\omega}\right)_{\omega=\zeta_0-E_N}\right] +\frac{4}{9}\frac{\Delta^2}{N(\zeta_0-E_P)}\left(\frac{dN}{d\omega}\right)^2_{\omega=\zeta_0-E_P}E_P^2\left[1-\frac{1}{2}\frac{\Delta}{N(\zeta_0-E_P)}\left(\frac{dN}{d\omega}\right)_{\omega=\zeta_0-E_P}\right], \quad (24)$$

and

$$\Delta C'(0)=\frac{1}{4}\frac{\Delta^2}{N(\zeta_0-E_N)}\left(\frac{dN}{d\omega}\right)^2_{\omega=\zeta_0-E_N}E_N^2\left[1-\frac{1}{2}\frac{\Delta}{N(\zeta_0-E_N)}\left(\frac{dN}{d\omega}\right)_{\omega=\zeta_0-E_N}\right]+\frac{2}{3}\frac{\Delta^2}{N(\zeta_0-E_H)}\left(\frac{dN}{d\omega}\right)^2_{\omega=\zeta_0-E_H}E_H^2\left[1-\frac{1}{2}\frac{\Delta}{N(\zeta_0-E_N)}\left(\frac{dN}{d\omega}\right)_{\omega=\zeta_0-E_N}\right]. \quad (25)$$

For the face-centered cubic lattice, referring to Fig. 2,

$$\Delta C(0)=\frac{4}{9}\frac{\Delta^2}{N(\zeta_0-E_L)}\left(\frac{dN}{d\omega}\right)^2_{\omega=\zeta_0-E_L}E_L^2\left[1-\frac{1}{2}\frac{\Delta}{N(\zeta_0-E_L)}\left(\frac{dN}{d\omega}\right)_{\omega=\zeta_0-E_L}\right], \quad (26)$$

and

$$\Delta C'(0)=\frac{2}{3}\frac{\Delta^2}{N(\zeta_0-E_X)}\left(\frac{dN}{d\omega}\right)^2_{\omega=\zeta_0-E_X}E_X^2\left[1-\frac{1}{2}\frac{\Delta}{N(\zeta_0-E_X)}\left(\frac{dN}{d\omega}\right)_{\omega=\zeta_0-E_X}\right]+\frac{2}{75}\frac{\Delta^2}{N(\zeta_0-E_W)}\left(\frac{dN}{d\omega}\right)^2_{\omega=\zeta_0-E_W}E_W^2\left[1-\frac{1}{2}\frac{\Delta}{N(\zeta_0-E_W)}\left(\frac{dN}{d\omega}\right)_{\omega=\zeta_0-E_W}\right]. \quad (27)$$

B. Temperature Effects

The free energy difference between the normal and superconducting states, $\Delta F(T)$, may be obtained from the BCS theory as

$$\Delta F(T)=N(0)(\hbar\omega_c)^2\{[1+(\Delta/\hbar\omega_c)^2]^{1/2}-1\}-\tfrac{1}{2}T[S_n(T)-S_s(T)], \quad (28)$$

where $\hbar\omega_c$ is the lattice vibrational energy, and $S_n(T)$ and $S_s(T)$ represent the entropy in the normal and superconducting states, respectively. In the weak-coupling limit $\Delta\ll\hbar\omega_c$, and thus we may approximate Eq. (28) by

$$\Delta F(T)=\tfrac{1}{2}n_c\Delta-\tfrac{1}{2}T\Delta S. \quad (29)$$

The temperature dependence of the energy gap is obtained from the BCS theory, as shown in Fig. 3. As seen from Fig. 3, the gap width changes very slowly as T increases from zero until $T\approx\frac{1}{2}T_c$, where T_c is the superconducting critical temperature. It then begins to fall more rapidly, approaching zero with a vertical tangent at T_c. Thus between zero and $\frac{1}{2}T_c$, the first term on the right in Eq. (29) is essentially independent of temperature. The entropy of the superconducting and normal states may be expressed in the usual way in terms of the probability of occupancy, which are randomly distributed over an ensemble. Thus,

$$S=-4k\sum_k f_k\ln f_k+(1-f_k)\ln(1-f_k), \quad (30)$$

where in the superconducting state the summation runs over all k greater than k_F at the Fermi level, and

$$f_k=1/e^{\beta E_k}+1, \quad (31)$$

where $\beta=1/kT$, and $E_k=(\omega_k^2+\Delta_k^2)^{1/2}$. In the normal state E_k is replaced by ω_k in Eq. (31) and the summation runs over all ω_k greater than zero. Thus,

$$TS_s=\frac{4N(0)}{\beta^2}\int_{\beta\Delta}^{\infty}\frac{2\epsilon^2-\epsilon_0^2}{(\epsilon^2-\epsilon_0^2)^{1/2}}f(\epsilon)d\epsilon, \quad (32)$$

where $\epsilon=\beta E$ and $\epsilon_0=\beta\Delta$. The entropy of the normal state is obtained as

$$TS_n=\frac{4N(0)}{\beta^2}\int_0^{\infty}2\alpha f(\alpha)d\alpha=\tfrac{2}{3}(\pi kT)^2N(0), \quad (33)$$

where $\alpha=\beta\omega$. At temperatures below $\frac{1}{2}T_c$, the superconducting entropy is almost negligible and thus the temperature dependence of the free energy difference is determined almost entirely by the temperature dependence of the entropy in the normal state. Thus between $T=0$ and $\frac{1}{2}T_c$, we may approximate $\Delta M(T)$ as

$$\Delta M(T)=\Delta M(0)-\tfrac{1}{2}(\pi kT)^2[d^2N(0)/dX^2]_0. \quad (34)$$

Near the critical temperature, the superconducting en-

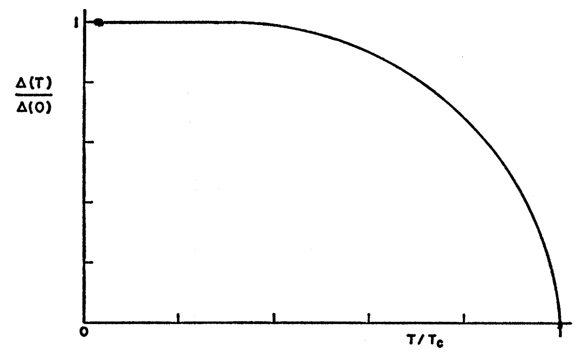

FIG. 3. Temperature dependence of the energy gap.

tropy approaches the entropy of the normal state. By differentiation of Eq. (30), we find for the strain dependence of the superconducting entropy

$$T\left(\frac{dS_s}{dX}\right)_T=-4\beta\sum_k f_k(1-f_k)E_k\left(\frac{dE_k}{dX}\right). \quad (35)$$

Now

$$E_k(dE_k/dX)=\Delta_k(d\Delta_k/dX)+\omega_k(d\omega_k/dX). \quad (36)$$

At $T=T_c$, $\Delta=0$, $E_k=\omega_k$, $f(\beta E)=f(\beta\omega)$ and

$$T_c\left(\frac{d\Delta S}{dX}\right)_{T=T_c}=4\beta\sum f_{kn}(1-f_{kn})\Delta_k\left(\frac{d\Delta_k}{dX}\right)=2N(0)\Delta\left(\frac{d\Delta}{dX}\right). \quad (37)$$

From Eqs. (8) and (29), at T_c

$$(d\Delta F/dX)_{T=T_c}=0, \quad (38)$$

even in the strained state. Further differentiation of Eqs. (29) and (35) shows that

$$(d^2\Delta F/dX^2)_{T=T_c}=0, \quad (39)$$

and therefore the difference in the elastic shear constants at the critical temperature disappears.

The energy gap near T_c may be approximated by the relation[4]

$$\Delta(T)\approx 3.2kT_c[1-(T/T_c)]^{1/2}. \quad (40)$$

In accordance with predictions of the BCS theory, and thermodynamic considerations, the free-energy difference, the internal energy difference and the entropy difference between the normal and superconducting states disappear at the critical temperature. As shown by Eq. (39), the second derivative of the free-energy difference with respect to shear strains, and hence the difference in shear constants, also disappear at the critical temperature. In addition, the energy gap at $T=T_c$ is zero, from Eq. (40). Such is not the case for the second derivative of the entropy difference with respect to shear strains at T_c. Substitution of the relation[4] that at absolute zero $\Delta(0)=1.76kT_c$ into Eq. (40) and differentiation of Eq. (40) with respect to shear strains, provides the relation in conjunction with Eqs. (9)–(11) and (37), that at the critical temperature

$$KT_c(d^2\Delta S/dX^2)_{T=T_c}=6.6\Delta M(0), \quad (41)$$

where $\Delta M(0)$ represents ΔC or $\Delta C'$ at absolute zero, and the constant K is defined in the first part of this section as either $\frac{1}{3}$ or $\frac{3}{4}$.

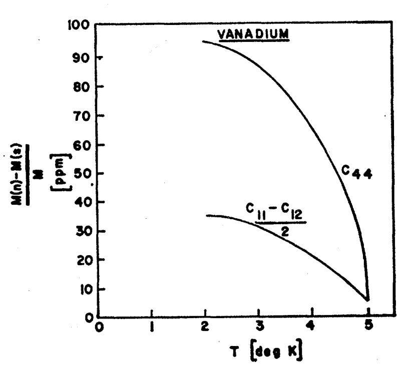

FIG. 4. The difference in the elastic shear constants of vanadium between the normal and superconducting states as a function of temperature.

3. COMPARISON WITH EXPERIMENT: VANADIUM AND NIOBIUM

The difference in the elastic shear constants of vanadium and niobium between the normal and superconducting states as a function of temperature have been measured by Alers and Waldorf.[2] The results are shown in Figs. 4 and 5. The experimental quantities necessary for a semiquantitative evaluation of Eqs. (22) and (23) are listed in Table I. Unfortunately, no information is available for niobium concerning $(dN/d\omega)$ and ζ_0. However, since the density of states of niobium is quite close to that of vanadium, we will approximate these values for niobium by those for vanadium. In these calculations, we will assume that E_N, E_H, and E_P may be approximated by ζ_0 and use the relation at absolute zero[4] that $\Delta=1.76kT_c$. Although we know the total density of states at the Fermi level[9–12] and can approximate the slope from the work of Cheng *et al.*[9] on T_i-V and V-Cr alloys, we cannot, at present, determine the individual contributions from symmetry points N, P, and, H in Eqs. (24) and (25). However, in order to show that the analysis presented in Sec. 2 is capable of giving the right order of magnitude when compared to the experimental values, we will assume without any theoretical justification that there are no contributions from symmetry points P and H in Fig. 1. The comparison between the values calculated from Eqs. (24) and (25) and the data in Table I with the experimental quantities[2] are given in Table II.

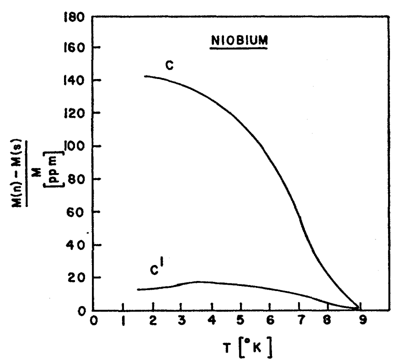

FIG. 5. The difference in the elastic shear constants of niobium between the normal and superconducting states as a function of temperature.

[9] C. H. Cheng, C. T. Wei, and P. A. Beck, Phys. Rev. **120**, 426 (1960).
[10] C. H. Cheng, K. P. Gupta, E. C. Van Reuth, and P. A. Beck, Phys. Rev. **126**, 2030 (1962).
[11] K. Clusius, P. Franzoni, and U. Z. Piesbergen, Z. Naturforsch. **15a**, 728 (1960).
[12] C. Chou, D. White and H. L. Johnston, Phys. Rev. **109**, 788, 797 (1958).

4. DISCUSSION AND CONCLUSIONS

The theory of superconductivity developed by Bardeen, Cooper, and Schrieffer,[4] in conjunction with the quantum-mechanical theory of elasticity developed by Fuchs,[5] Leigh,[6] and others,[7,8] has been shown to be capable of presenting a model by which the difference in elastic shear constants and the shear strain dependence of the critical temperature and critical field may be interpreted.

On the basis of this model the difference in elastic shear constants between the normal and superconducting states arises from a similar electron transfer mechanism, containing terms in E^2, which is the dominant contribution determining the electron contribution to the temperature dependence of the elastic shear constants in the normal state.[1]

For the case of vanadium, and perhaps niobium, the second term in square brackets in Eq. (22) is negligible compared to one, and hence the difference in elastic shear constants and the second derivatives of the free energy difference at absolute zero for vanadium should

TABLE I. Experimental quantities used to calculate the shear strain dependence of the free energy, critical temperature, and critical field.

Quantity	Vanadium	Niobium	Reference
V ($T=0$°K)	8.32 cm³	10.75 cm³	a
T_c	5.1°K	9.2°K	2
$N(0)$	1.95 eV⁻¹ atom⁻¹	1.60 eV⁻¹ atom⁻¹	9–12
$(dN/d\omega)_{\omega=0}$	−3.85 eV⁻² atom⁻¹	···	9, 10
ζ_0	7.74 eV	···	b

[a] G. K. White, Cryogenics 2, 292 (1962).
[b] H. W. B. Skinner, Phil. Mag. 45, 1070 (1954).

exhibit positive values irrespective of the sign of the slope of the density of states and the change in energy of symmetry points with shear strain. This is due to the appearance of these terms to the second power in Eq. (22). Such may not be the case for the sum of the second derivatives of the energy gap with respect to shear strains, given by Eq. (21), in which the slope of the density of states enters to the third power. As a consequence, Eq. (21) may exhibit positive or negative values dependent on the sign of the individual $(dN_i/d\omega)$.

In addition, the first derivatives of the energy gap with respect to shear strain, given by Eq. (18), may exhibit positive or negative values dependent on the sign of the product of the individual $(dN_i/d\omega)$ and the $(dE_i/dX)_0$. It should be remembered[1,6–8] that for a given type of symmetry point $(dE_i/dX)_0$ may be positive or negative dependent on the relative shift of the specific zone face towards or away from the origin during shear. Of course, according to the model developed in Sec. 2, the sum of the first derivatives of the energy gap with respect to shear strain at zero strain is identically zero.

TABLE II. The difference in elastic shear constants between the normal and superconducting states at absolute zero in units of dyn/cm².

Element	Modulus	Calculated[a]	Experimental
V	ΔC	1.57×10^7	4.7×10^7
	$\Delta C'$	0.885×10^7	2.1×10^7
Nb	ΔC	4.84×10^7	4.6×10^7
	$\Delta C'$	2.42×10^7	0.84×10^7

[a] Calculated on the basis of no contribution from symmetry points P and H.

The free energy difference at absolute zero[2] for vanadium is 7.2×10^4 erg cm^{-3} and for niobium 15×10^4 erg cm^{-3}. The measured difference in elastic shear constants, however, is two to three orders of magnitude greater ($\sim10^7$ erg cm^{-3}) than the free energy difference. The calculations performed in Sec. 3 are intended to show that the model developed in Sec. 2 is capable of presenting the correct order of magnitude for the elastic shear constants of vanadium and niobium. As mentioned previously, the assumption of contributions only from symmetry points N in Fig. 1 is without any theoretical justification. The experimental values for vanadium in Table II show, however, that ΔC is approximately twice $\Delta C'$ at absolute zero. This indicates, from Eqs. (24) and (25), that there are contributions from symmetry points N only or that the contribution from symmetry points P is twice as large as from symmetry points H. For niobium, however, ΔC is more than five times as large as $\Delta C'$ at absolute zero. In addition the energy gap of niobium is almost twice as large as that for vanadium and the closeness of the values of ΔC for both vanadium and niobium listed in Table II would be rather surprising if one assumed the same Fermi surface for niobium as for vanadium. On the basis of the model developed in Sec. 2 and the values listed in Table II, one must assume a rather different Fermi surface for these two metals, even though it is generally assumed that they possess the same number of s and d electrons and their electron densities of states lie quite close together.

The analysis of temperature effects, presented in Sec. 2, reveals the qualitative features exhibited by the experimental curves of Figs. 4 and 5, disregarding the anomalous dip in the curve of $\Delta C'$ for niobium which is thought to be due to impurity effects.[3] In general the T^2 dependence is evident below $\frac{1}{2}T_c$ in accordance with Eq. (34) and the difference in shear moduli disappears at the critical temperature, in accordance with Eq. (39). Although the energy gap and second derivative of the free energy difference disappear at the superconducting critical temperature, it is found that the second derivative of the entropy difference between the normal and superconducting state at the critical temperature is finite, and is given by Eq. (41) in terms of the difference in elastic shear constants at absolute zero.