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Transition Metals and the Fröhlich Mechanism for Superconductivity

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The properties of screened plasma oscillations of the *d* band, which Fröhlich first suggested could lead to superconductivity, are investigated. Specific-heat anomalies in the normal and superconducting state, normal-state resistivities, pressure-induced and pressure-dependent superconductivity, Mössbauer-effect studies, lattice transformations, and the occurrence of superconductivity in transition metals are compared with the theory. These diverse properties indicate that the Fröhlich mechanism is operative in high-T_c transition elements and constitutes a new mechanism for superconductivity.

I. INTRODUCTION

Perhaps the most important unresolved question in superconductivity (other than the existence of room-temperature superconductivity) is whether mechanisms other than the electron-phonon one exist. Recently, Matthias[1] has pointed out that there appear to be at least four classes of superconductors and perhaps four different mechanisms which cause superconductivity. The classes are (i) the nontransition metals which have *s* and *p* conduction electrons, (ii) transition metals with partially filled *d* shells and *s* electrons in the conduction band, (iii) *f* elements with a partially filled *f* shell, and (iv) high-Debye-temperature metals, mainly borides and beryllium compounds. Only in class (i) is the electron-phonon mechanism clearly established.

While various nonphonon mechanisms have been proposed, Schrieffer[2] has pointed out that all the mechanisms (phonon included) correspond to a dielectric anomaly. Hence, by looking carefully at the dielectric constant $\epsilon(\vec{q}, \omega)$ one can hope to uncover new mechanisms if they exist. Recently, Fröhlich[3] has treated the dielectric constant for metals with incomplete inner shells and found a region of q and ω which provides an attractive interaction between electrons. Physically the interaction is quite similar to the electron-phonon interaction, but instead of phonons, which are a collective mode of the ions, one has a collective electronic mode. This mode consists of the screened plasma oscillations of the inner (*d* or *f*) bands. The screening is provided by *s* or *p* electrons. Throughout this paper we shall refer to the screened plasma oscillations as acoustic plasmons since their ω-versus-q dispersion relation is linear at low q. The screening electrons will be called *s* electrons and the inner-band electrons will be referred to as *d* electrons, although the same analysis will hold for *f* electrons.

The Fröhlich model attempts to account for the behavior associated with classes (ii) and (iii) cited above. The mechanism suggested by Fröhlich is not really new, since it has been known for some time that the dielectric treatment for the phonon mechanism would hold just as well if the ion system were replaced by electrons or holes from another band.[4] The virtues of the Fröhlich mechanism are (a) that it predicts the existence of a new acoustic mode which one can hope to detect by means other than superconductivity and (b) it makes predictions about the dependence of the transition temperature on various physical parameters which one can also hope to check against experiment.

In this paper we consider some of the properties, both normal and superconducting, that a system satisfying the conditions for acoustic plasmons should manifest. A comparison of the predicted properties and known experimental results indicates that the acoustic plasmons are present in many of the transition-metal superconductors.

In Sec. II we review Fröhlich's derivation of the acoustic plasmon modes and also some extensions of his theory to include lifetime effects and phonon modes. Section III contains a calculation of the specific heat due to the acoustic plasmons as well as a comparison with experimental results. In Sec. IV the resistivity of transition metals is briefly discussed. Section V is devoted to a comparison of the criterion for superconductivity via the acoustic plasmons and the occurrence of superconductivity in the transition metals. Section VI gives an account of the expected pressure dependence of T_c. Section VII relates the anomalous Mössbauer effect in Nb_3Sn, and the lattice transformation in Nb_3Sn to the acoustic plasmons. The discussion in Sec. VIII analyzes and summarizes our results.

II. FRÖHLICH MODEL

In this section we review Fröhlich's derivation of the acoustic plasmon modes, and also consider some extensions of his theory to include lifetime effects and phonon modes.

The starting point for Fröhlich's derivation is an expression for the longitudinal dielectric constant $\epsilon(q,\omega)$ of the system. Using the expression

$$\epsilon(\vec{q},\omega)=\epsilon_0(\vec{q},\omega)+4\pi(\alpha_s+\alpha_d+\alpha_L), \tag{2.1}$$

where $\alpha_i (i=s,d)$ is the polarizability due to "free" electron properties of i electrons and α_L that due to the lattice. $\epsilon_0(\vec{q},\omega)$ contains all other contributions, particularly those connected with band-to-band electronic transitions.

Using Lindhard's[5] expressions for α_i in appropriate limits, one has

$$4\pi\alpha_i=3\omega_{0i}^2 f_{0i}/q^2v_i^2+\cdots \quad \text{if } q^2v_i^2>\omega^2, \tag{2.2}$$

$$4\pi\alpha_1=-\omega_{0i}^2 f_{0i}/\omega^2+\cdots \quad \text{if } q^2v_i^2<\omega^2, \tag{2.3}$$

where f_{0i} is the oscillator strength, v_i the Fermi velocity, and

$$\omega_{0i}^2=4\pi e^2 n_i/m, \tag{2.4}$$

with n_i the density of electrons, gives the unscreened plasma frequencies. In the frequency region for which $\alpha_s>0$ and $\alpha_d<0$, one has

$$\epsilon(q,\omega)=\epsilon_0(q,\omega)+\frac{3\omega_{0s}^2 f_{0s}}{q^2v_s^2}-\frac{\omega_{0d}^2 f_{0d}}{\omega^2}+4\pi\alpha_L, \tag{2.5}$$

if

$$q^2v_d^2<\omega^2<q^2v_s^2. \tag{2.6}$$

In (2.5), α_L can be neglected compared with α_d as long as $\omega^2>q^2v_d^2$; we shall include α_L subsequently.

The longitudinal frequencies $\omega_p(q)$ of the system are obtained from the condition

$$\epsilon(\vec{q},\omega_p)=0. \tag{2.7}$$

Neglecting the ω dependence of ϵ_0, one obtains

$$\omega_p^2=\frac{q^2\omega_{0d}^2 f_{0d}}{q^2\epsilon_0(q)+3\omega_{0s}^2 f_{0s}/v_s^2}, \quad q^2v_d^2<\omega_p^2<q^2v_s^2. \tag{2.8}$$

This expression is the dispersion relation for the acoustic plasmons. The maximum wave number q_m and frequency are obtained from this expression and are given by

$$\omega_{p,m}^2=q_m^2v_d^2=\omega_{0d}^2 f_{0d}\gamma_F^2=[4\pi e^2N_d(E_F)/3]\gamma_F^2v_d^2. \tag{2.9}$$

Here one has

$$\gamma_F^2=\frac{1}{\epsilon_0(q_m)}\left(1-3\frac{N_s(E_F)}{N_d(E_F)}\right), \tag{2.10}$$

where $N_i(E_F)$ is the density of states near the Fermi surface in the ith band. To obtain (2.9) and (2.10), the mean Fermi velocities have been defined by the relation

$$mv_i^2=3f_{0i}n_i/N_i(E_F). \tag{2.11}$$

Here we note that if the effective-mass approximation is valid in the occupied part of the bands, then f_{0i} is independent of n_i; f_{0i} vanishes for full bands.

From the above considerations one sees that for the existence of the acoustic plasmons the following condition must be satisfied:

$$\frac{v_d^2}{v_s^2}=\frac{N_s(E_F)}{N_d(E_F)}\frac{(n_df_{0d})}{(n_sf_{0s})}<1 \tag{2.12}$$

and

$$\gamma_F^2>0. \tag{2.13}$$

To obtain superconductivity from these ideas, Fröhlich wrote the effective interaction between electrons as

$$H_{\text{int}}=\sum_{\vec{q}}\frac{4\pi e^2}{q^2V}\rho(q)\sum_\omega\frac{\rho(q,\omega)}{\epsilon(q,\omega)}. \tag{2.14}$$

Here V is the volume, $\rho(q)$ is the qth Fourier component of electronic density, and $\rho(q,\omega)$ the fraction with frequency ω. Using (2.5) (neglecting α_L) and (2.8), one can write the following for $\epsilon(q,\omega)$:

$$\epsilon(q,\omega)=\epsilon_1(q)[1-(\omega_p^2/\omega^2)], \quad q^2v_d^2<\omega^2<q^2v_s^2 \tag{2.15}$$

where

$$\epsilon_1(q)=\epsilon_0+(3\omega_{0s}^2f_{0s}/q^2v_s^2), \quad q^2v_d^2<\omega^2<q^2v_s^2 \tag{2.16}$$

is the dielectric constant when the contribution of the d electrons is neglected. The interaction (2.14) can be written explicitly using (2.15) in the form $1/\epsilon=(1/\epsilon-1/\epsilon_1)+1/\epsilon_1$:

$$H_{\text{int}}=\sum_{\vec{q},\omega}\frac{4\pi e^2\rho(q)\rho(q,\omega)}{Vq^2\epsilon_1(q)}\left(\frac{\omega_p^2}{\omega^2-\omega_p^2}+1\right). \tag{2.17}$$

For $\omega^2<\omega_p^2$, the first term represents the ω_p plasmon-induced attraction (if $q^2v_d^2<\omega^2<q^2v_s^2$), while the second term represents the Coulomb repulsion screened by ϵ_1, which is valid in this region.

Only the components of $\rho(q,\omega)$, which satisfy (2.6), are to be kept in (2.17). These include (s-s) and mixed (d-s) density components, but most (d-d) terms are excluded. Assuming $N_d(E_F)\gg N_s(E_F)$ [(2.10) and (2.13) require $N_d(E_F)>3N_s(E_F)$], only the mixed (d-s) term is retained. Applying the Bardeen-Copper-Schrieffer (BCS) formulation[6] of superconductivity, Fröhlich obtained an interaction constant F given by

$$F=2[4\pi e^2/q_m^2\epsilon_1(q_m)][N_s^*(E_F)N_d^*(E_F)]^{1/2}. \tag{2.18}$$

Here $N_i^*(E_F)$ is given by $N_i(E_F)$ multiplied by the fraction of the i Fermi surface available for transitions. Noting that $[\epsilon_1(q_m)]^{-1}=\gamma_F^2$, the final expression for F is

$$F=\frac{2\delta^{1/2}}{\pi}\frac{e^2}{\hbar(v_sv_d)^{1/2}}\gamma_F^2, \tag{2.19}$$

where δ is the degeneracy of the d band. An alternate expression for F is (with a the Bohr radius)

$$F=\frac{2\delta^{2/3}}{\pi(3\pi^2)^{1/3}}\frac{1}{\epsilon_0}\frac{1}{(n_d n_s)^{1/6}}\frac{1}{a}\left[1-\frac{3}{\delta^{2/3}}\frac{f_{0d}}{f_{0s}}\left(\frac{n_s}{n_d}\right)^{1/3}\right]. \quad (2.20)$$

In this form, conditions (2.12) and (2.13) become

$$\frac{3}{\delta^{2/3}}\frac{f_{0d}}{f_{0s}}<\left(\frac{n_d}{n_s}\right)^{1/3}<\delta^{1/3}\frac{f_{0s}}{f_{0d}}. \quad (2.21)$$

At the lower limit, F vanishes; for increasing n_d (keeping n_s fixed), F reaches a maximum at $n_{d,m}$ and then decreases again. The value $n_{d,m}$ is given by

$$(n_{d,m}/n_s)^{1/3}=9f_{0d}/\delta^{2/3}f_{0s}. \quad (2.22)$$

In analogy with the BCS theory, the transition temperature is given by

$$kT_c=\hbar\omega_{p,m}e^{-1/F}, \quad (2.23)$$

if one assumes that the acoustic plasmon interaction predominates over any phonon interaction.

Before considering the effects of the existence of the acoustic plasmons on the properties of transition metals, we consider what changes including lifetimes and mean free paths will entail and also the inclusion of α_L. First we consider lifetime effects.

Kliewer and Fuchs[7] have recently discussed how lifetimes and mean free paths should enter the Lindhard expressions. Using the Kliewer-Fuchs constant lifetime expressions, we find that (2.5) becomes

$$\epsilon(q,\omega,\tau,l)=\epsilon_0(q,\omega)+\frac{3\omega_{0s}^2 f_{0s}ql_s}{q^2v_s^2(ql_s-\tan^{-1}ql_s)}-\frac{\omega_{0d}^2 f_{0d}}{\omega^2-i\omega/\tau_d}+4\pi\alpha_L, \quad (2.24)$$

where l_s is mean free path for s electrons and τ_d a lifetime for d electrons. Following Fröhlich we assume that α_L can be dropped and find that $\epsilon(q,\omega_p,\tau,)=0$ yields a solution with real and imaginary parts given by

$$\mathrm{Im}\omega_p=-\tfrac{1}{2}\tau_d \quad (2.25)$$

and

$$\mathrm{Re}\omega_p=\left(\frac{\omega_{0d}^2 f_{0d}q^2}{q^2\epsilon_0(q)+3\omega_{0s}f_{0s}/v_s^2 g(ql)}-\frac{3}{4\tau_d^2}\right)^{1/2}, \quad (2.26)$$

where

$$g(q)=(ql-\tan^{-1}ql)/ql\geq 0.$$

For $\tau_d\to\infty$, we regain undamped waves. The ql correction is small until $ql\ll 1$ and, hence, we can write

$$\mathrm{Re}\omega_p=\omega_{p,0}(q)(1-3/4\omega_{p,0}^2(q)\tau_d^2)^{1/2}, \quad (2.27)$$

where $\omega_{p,0}(q)$ is the undamped Fröhlich solution. As long as $\omega_p\tau_d\gg 1$, the results are essentially unchanged from the undamped case. In the constant lifetime approximation, however, as $q\to 0, \omega_{p,0}\to 0$, and hence below some value of $q=q_0$ there are no solutions. If τ_d becomes too short, such that $\omega_{p,m}\tau_d<1$, there will be no range of q for which the acoustic plasmon is a valid elementary excitation. If τ_d varies with temperature, then there may be a temperature above which the acoustic plasmons cease to exist as well defined entities. To determine τ_d we need to know the dominant scattering mechanism for the d electrons. At low temperatures, impurity scattering dominates; at higher temperatures either s-d scattering or phonon scattering should dominate.[8,9] If we assume a simple kinetic approach then $l=1/N_i\sigma$, where σ is a scattering cross section and N_i a number density. The expression $\tau=l/v$ can then be used for either s or d electrons. We can estimate l from the resistivity which involves the s electrons primarily and then use this to obtain $\tau_d=l/v_d$. Using this approach we find that for Nb the acoustic plasmons could exist for a large range of q up to room temperature, while for Nb_3Sn the mode should be washed out below room temperature.

We thus expect that while lifetime effects may influence transport properties and perhaps T_c, the acoustic plasmon remains a valid excitation of the system essentially unchanged from Fröhlich's treatment.

To treat the plasmons and phonons simultaneously, we note that from (2.5) retaining α_L we should obtain two solutions from $\epsilon(q,\omega)=0$, one corresponding to the longitudinal phonons, the other to the plasmons. The polarizability of the lattice is given by [4,10]

$$4\pi\alpha_L=-\omega_m^2/(\omega^2-\Omega^2), \quad (2.28)$$

where

$$\omega_m^2=4\pi Nz^2e^2/M \quad (2.29)$$

is the ion plasma frequency, z the valence, and the "core frequency" is

$$\Omega^2=(B_{\mathrm{core}}/MN)q^2, \quad (2.30)$$

with B_{core} being the bulk modulus due to the repulsion of the ion cores and N is the density. Setting $\epsilon(q,\omega)=0$ yields the equation

$$\omega^4-\omega^2\left(\frac{(\omega_{0d}^2 f_{0d}+\omega_m^2)}{\epsilon_1(q)}+\Omega^2\right)+\frac{\Omega^2\omega_{0d}^2 f_{0d}}{\epsilon_1(q)}=0, \quad (2.31)$$

with solutions

$$\omega^2=\frac{1}{2}\left\{\left[\frac{\omega_{0d}^2 f_{0d}+\omega_m^2}{\epsilon_1(q)}+\Omega^2\right]\pm\left[\left(\frac{\omega_{0d}^2 f_{0d}+\omega_m^2}{\epsilon_1(q)}\Omega^2\right)^2-\frac{4\Omega^2\omega_{0d}^2 f_{0d}}{\epsilon_1(q)}\right]^{1/2}\right\}. \quad (2.32)$$

Rearranging terms under the square root gives

$$\omega^2=\frac{1}{2}\left\{\left[\frac{\omega_{0d}^2 f_{0d}+\omega_m^2}{\epsilon_1(q)}+\Omega^2\right]\right.$$
$$\left.\pm\left[\left(\Omega^2+\frac{\omega_m^2}{\epsilon_1(q)}-\frac{\omega_{0d}^2 f_{0d}}{\epsilon_1(q)}\right)^2+\frac{4\omega_m^2\omega_{0d}^2 f_{0d}}{\epsilon_1^2(q)}\right]^{1/2}\right\}. \quad (2.33)$$

If Ω^2 is large compared to $\omega_{0d}^2 f_{0d}/\epsilon_1(q)$ and $\omega_m^2/\epsilon_1(q)$, then the last term under the square root can be dropped and the solutions become

$$\omega^2=\Omega^2+\omega_m^2/\epsilon_1(q) \quad (2.34)$$

and

$$\omega^2=\omega_{0d}^2 f_{0d}/\epsilon_1(q). \quad (2.35)$$

The first is the dispersion relation for the longitudinal phonons, while the second is just the acoustic plasmon mode since (2.35) is identical to (2.8).

There are other possible choices for α_L which can lead to modes with mixtures of lattice and plasmon parameters. While such couplings may be present in some systems, we shall assume throughout our work that the phonons and acoustic plasmons comprise two separate independent excitation modes of the system as indicated by (2.34) and (2.35). As such, they can each contribute to the specific heat, they each constitute a scattering mechanism for electrons, and each may contribute to the interaction causing superconductivity.

Under the assumption that the acoustic plasmon interaction dominates in producing superconductivity, Fröhlich[3] pointed out that the variation of T_c with the filling of the d shells would agree with Matthias's rules.[11] This comes about from the fact that $\omega_{p,m}$, as given in (2.9), varies with the effective number of free d electrons, $n_d f_{0d}$, which increase proportionally with n_d for nearly empty bands and reach a maximum to become zero again for full bands. Assuming that the fivefold degenerate bands are split into twofold and threefold degeneracies, $\omega_{p,m}$ represents a curve similar to Matthias's curve of the dependence of T_c on the filling of the d shell. The isotope effect would also be absent for an acoustic plasmon superconductor, since $\omega_{p,m}$ is independent of the ion mass. In general, however, if both the electron-phonon and acoustic plasmon mechanisms are operative, some isotope effect should exist.

III. SPECIFIC HEAT

If an additional acoustic mode exists in a system, its presence should be seen in specific-heat measurements. There are a number of anomalies which have been seen in low-temperature specific-heat measurements of transition metals, and we now consider to what extent Fröhlich's acoustic plasmons can explain the observed behavior.

The specific heat associated with the acoustic plasmons should be similar to that associated with acoustic lattice phonons. The main differences lie in the fact that (a) the plasmons have only one branch (longitudinal) while the phonons have three, (b) the number of degrees of freedom per unit volume associated with the phonons is $3N$, while that associated with the plasmons is determined by q_m, and (c) in place of a Debye temperature there is a temperature θ_1 defined by $k\theta_1=\hbar\omega_{p,m}$. Our approach is to write the contribution to the specific heat from the acoustic plasmons in terms of that due to the acoustic phonons. This will facilitate comparisons with experimental data.

Assuming a constant Debye temperature Θ for the phonons and using the Debye theory[12] for the lattice specific heat, one has the result shown in Fig. 1. The specific heat of the acoustic plasmons will follow an identical curve if we assume the velocity is independent of q, but with θ_1 replacing Θ and $f3R$ replacing $3R$. Here f determines the number of modes associated with the acoustic plasmons and is given by

$$f=\tfrac{1}{3}(q_m/Q_D)^3, \quad (3.1)$$

where $Q_D^3=6\pi^2 N$ and N is the number of atoms per unit volume for a monotonic system and the number of unit cells per unit volume for alloys or compounds. The sum of the specific heat of the acoustic plasmons and acoustic phonons is given by

$$C(T)=C_D(\Theta/T)+fC_D(\theta_1/T), \quad (3.2)$$

where C_D is the theoretical Debye specific-heat function. The quantity $\Theta C/3RT$ at low temperatures is plotted in Fig. 2 for several values of the parameters f, and $\phi=\Theta/\theta_1$. The curves of Fig. 2 were obtained from the tabulated values of $\Theta C_D(\Theta/T)/3RT$ by the relation

$$\frac{\Theta C}{3RT}=\left(\frac{\Theta C_D(\Theta/T)}{3RT}\right)_{\text{Table}}+f\phi\left(\frac{\theta_1 C_D(\Theta/\phi T)}{3RT}\right)_{\text{Table}}. \quad (3.3)$$

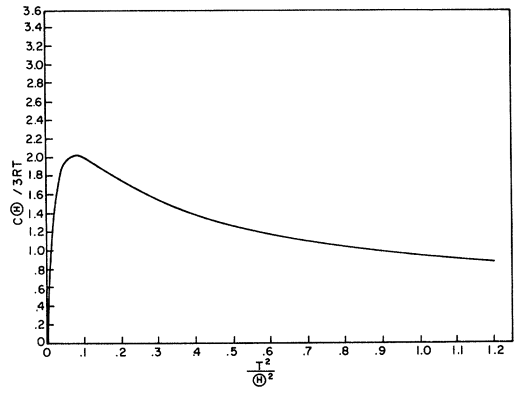

FIG. 1. Specific heat of the acoustic modes from the Debye theory.

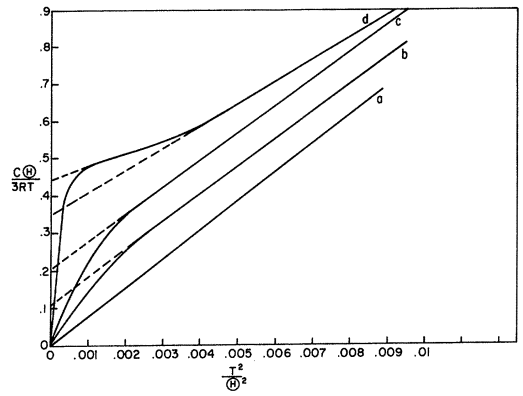

FIG. 2. Sum of the lattice specific heat, with Debye temperature Θ and high-temperature limit $3R$, and the specific heat of another acoustic mode, with Debye temperature θ_1 and high-temperature limit $3Rf$. (a) $f=0$ (lattice alone); (b) $f=0.01$, $\Theta/\theta_1=5$; (c) $f=0.02$, $\Theta/\theta_1=5$; (d) $f=0.02$, $\Theta/\theta_1=10$.

Several things should be noted about Figs. 1 and 2. There is a factor of 10^2 difference in the horizontal scale, so that Fig. 2 is in a region of T in which the Debye specific heat of the lattice should go[13] as T^3, as illustrated by curve a. In Fig. 1 the maximum occurs at roughly $T^2/\Theta^2=0.075$, and is followed by a nearly linear region up to about $T^2/\Theta^2\approx 0.3$. In curves b, c, and d of Fig. 2 the deviations from straight lines are due to the maximum, as shown in Fig. 1, occurring for the acoustic plasmons, in the region of temperature where the phonons show T^3 behavior. In Fig. 2, curve a, which is the lattice alone, curve b which has $f=0.01$ and $\phi=5$, and curve c which has $f=0.02$ and $\phi=5$ all have essentially the same slope above the "break" points, while curve d which has $f=0.02$ and $\phi=10$ shows a different slope and a different type of "break".

Specific-heat data for metals is usually analyzed by noting that in the normal state the specific heat can be written at low temperature as

$$C=\gamma_e T+\beta T^3, \tag{3.4}$$

where $\gamma_e T$ is the electronic contribution and βT^3 that due to the lattice. The quantity γ_e is given by

$$\gamma_e=\pi^2 N(E_F)k^2/3, \tag{3.5}$$

with $N(E_F)$ the electron density of states (both spin) at the Fermi level. For β one writes

$$\beta=12\pi^4 Nk/5\Theta^3. \tag{3.6}$$

From a plot of C/T versus T^2 and (3.4), one expects a straight line with a $T=0$ intercept of γ_e and a slope which determines Θ.

For metals which become superconducting, especially those with high transition temperature, a problem arises in obtaining γ_e and Θ. In particular, for Nb_3Sn and V_3Si magnetic fields high enough to keep the sample normal far below T_c are not readily available and extrapolations are necessary to obtain γ_e. Here, in particular, one would expect that curvature in the low temperature C/T versus T^2 can make a significant difference in the value of γ_e deduced from extrapolated values of the specific heat. Thus, curves b, c, and d in Fig. 2, which do not include the usual $\gamma_e T$ electronic contribution to the specific heat, would nevertheless give an apparent γ_e if extrapolated from a point above the "break", i.e., the point at which the dashed lines intersect, the ordinate would appear to be an additional contribution to γ_e.

Experimental data on transition-metal elements and alloys exhibit behavior in some instances which points to the presence of acoustic plasmons. Morin and Maita[14] have measured the specific heats of a number of transition-metal alloys, elements, and compounds. They found for Nb and many of its alloys with Zr and Mo a change in the slope of C/T versus T^2 occurred at ~9.5 K independent of the transition temperature of the samples. The change in slope is similar to that seen in Fig. 2 for curves b and c. Their value of γ_e obtained from the higher-temperature curve is more than 50% higher than that obtained from the lower-temperature curve for Nb. Morin and Maita suggested that a rapid change in $N(E_F)$ with temperature might account for their results. Bucher, Heiniger, and Muller,[15] however, find that for Nb, while a gradual change in slope is evident in C/T versus T^2, there is no change in $N(E_F)$ as seen by magnetic susceptibility measurements. That a similar change in slope exists in Nb_3Sn has been suggested by Vieland and Wicklund.[16] They found in extrapolating their specific data from near T_c to $T=0$ that an excess entropy and a value of γ_e 60% higher than expected occur, unless the C/T-versus-T^2 curve bends downward somewhere below T_c.

Work in V_3Si also shows anomalous behavior. Kunzler *et al.*[17] have reported specific-heat data which has a pronounced dependence on stress, while Bonnerot *et al.*[18] found in four crystals of V_3Si with differing stoichiometry C/T-versus-T^2 curves which were parallel above T_c but vertically displaced from one another. The extrapolated values of γ_e varied over a factor of 2, while the T_c of all the samples was 17.1. Displaced curves with parallel slopes are just what one has in Fig. 2 for curves b and c which differ from each other only in the value of f, the number of modes in the acoustic plasmons. Whether V_3Si follows the pattern of curves b and c or that of d below T_c is not clear in absence of work in sufficiently high fields.

To illustrate what information might be available from specific-heat data, we consider the Morin-Maita data[14] for Nb. From the "break" in their

curve at $T \simeq 9.5$ we can find θ_1 by noting that the break is due to the maximum in C/T versus T^2 for the plasmons which occurs at $T^2/\theta_1^2 = 0.075$. We thus have that $\theta_1 \simeq 35$ K. The difference in the values of γ_e obtained from the high- and lower-temperature slopes was $\Delta\gamma_e = 4.2$ mJ/mole $(\mathrm{K})^2$. This quantity is directly related to f through the fact that above the maximum in the C_D/T-versus-T^2 curve a linear region exists which can be written as $y = b_0 + b_1 x$, where $y = C_D\Theta/3RT$, $x = (T/\Theta)^2$, $b_0 \simeq 2.24$, and $b_1 \simeq -2.32$. The relation for $\Delta\gamma_e$ is simply

$$\Delta\gamma_e = (f b_0/\theta_1)3R. \tag{3.7}$$

Hence

$$f = (\Delta\gamma_e/b_0 3R)\theta_1. \tag{3.8}$$

For Nb one finds that $f \simeq 2.6 \times 10^{-3}$. Equation (3.1) can now be used to determine q_m. One finds that $q_m \approx 0.2Q_D = 3 \times 10^7$ cm^{-1}. From (2.9), the relation $k\theta_1 = \hbar q_m v_d$ can be used to determine v_d, which gives $v_{d\mathrm{Nb}} \simeq 1.55 \times 10^5$ cm/sec. The second part of Eq. (2.9) can be used to obtain γ_F if one assumes that $N_d(E_F)$ is determined by (3.5). Using $N_d(E_F) \simeq 1.1 \times 10^{35}$/erg cm^3, one finds that $\gamma_{F,\mathrm{Nb}} = 0.09$, which is in accord with Fröhlich's expectation that $\gamma_F^2 \ll 1$.

A glance at (2.19) and (2.23) indicates that we now have all the parameters necessary to calculate T_c, except δ and v_s. The degeneracy of the d bands at the Fermi level we take to be unity, since the broadening of the band and the s-d admixing[8] will lift the atomic degeneracy which would ordinarily be two or three. (The spin degeneracy is not included in δ and is assumed to be two.) Mattheiss[19] has recently discussed the experimental and theoretical values for $\langle v^2 \rangle$ in Nb, but a value for v_s is unavailable. We can, however, use (2.19) and (2.23) to calculate $v_{s,\mathrm{Nb}}$ rather than T_c. With $T_c = 9.2$ K and $\theta_1 = 35$, Eq. (2.1) requires that $F_{\mathrm{Nb}} = 0.75$; this yields $v_s = 1.1 \times 10^7$ cm/sec. The experimental value of v deduced[19] from the value of temperature dependence at H_{c2} is 5.1×10^7 cm/sec and the theoretical value obtained from band-structure calculation is 6.2×10^7 cm/sec. Our value is in reasonable accord with these results since we have used the experimental electron specific heat to obtain $N_d(E_F)$, without consideration of possible contribution to γ_e from the s electrons and phonon enhancement effects. Since $v_s \propto N_d^{-2}$, the corrections could increase its value by as much as a factor of 4. In addition, if an attractive interaction via phonons is operative simultaneously, the resulting v_s could be still higher.

If we proceed in a similar manner for Nb_3Sn, we find $f \approx 2.5 \times 10^{-2}$, $\theta_1 \approx 44$ K, $q_m = 3.7 \times 10^7$ cm^{-1}, $v_d \approx 1.6 \times 10^5$, $\gamma_F = 0.092$, $F = 1.12$, and $v_s = 6.8 \times 10^6$ cm/sec. Here we have assumed a break point at ~12 K and a $\Delta\gamma_e$ indicated by the work of Vieland and Wicklund.[16] These results are subject to the same uncertainties cited in the case of Nb and an additional one due to the lack of an experimental break temperature.

The above discussion pertained to normal-state anomalies in the specific heat. There have been some results in the superconducting state which may also indicate the presence of acoustic plasmons. The specific-heat measurements of Shen, Senozan, and Phillips[20] and the thermal conductivity results of Carlson and Satterthwaite[21] on Nb both show anomalous behavior, one similar to curve b and the other to curve d of Fig. 2. The break in the curves, however, occurs well below the transition temperature in the range 0.1–0.3 K. If one interprets this effect in terms of the acoustic plasmons, one concludes that another d band exists with a small f and θ_1. While the plasmons associated with this band do not determine T_c, they should exhibit any of the other properties associated with plasmons. Several anomalies in V[22] and Ta[20] have also been reported.

Throughout this section we have discussed the specific heat that would be associated with acoustic plasmons and interpreted experimental results in terms of this model. Other explanations for the observed results have been given; rapid variation of the density of states with temperature,[14] the existence of soft lattice modes,[16] and lattice transformations[18] have been suggested for the anomalies seen in the normal state, while those in the superconducting state are attributed to the presence of a second energy gap.[22–24] Our analysis of this section indicates that the results obtained in various transition metals can all be understood on the basis of an additional acoustic excitation which has a relatively small characteristic temperature and a small number of degrees of freedom. Fröhlich's acoustic plasmons have the requisite properties, and by using Fröhlich's model one can obtain a value for v_d which to our knowledge is unavailable by other means.

IV. RESISTIVITY

It is known that the resistivity of the transition metals follow either a roughly T^3 law or a T^5 law at low temperatures.[25,26] Generally, the T^3 behavior occurs in the high density-of-states materials[25] [Sc, Y, Lu, V, Nb, Ta, (Tc), La, Pd, and Pt] and is ascribed to s-d scattering. The T^5 behavior occurs for low density-of-states elements (Ti, Zr, Hf, Mo, W, Re, Ru, Os, Ir, and Rh) and is ascribed to the usual electron-phonon scattering characteristic of the monovalent metals. In addition, the resistivity of Nb_3Sn has been studied quite thoroughly[27] and exhibits a quite anomalous behavior.

In the Fröhlich model the acoustic plasmons should act as an additional scattering mechanism. The calculation proceeds as for electron-phonon scattering but with the coupling given by essentially $(4\pi e^2/q^2\epsilon_0)^{1/2}$. Following Ziman,[9] Eq. (9.5.24), one finds neglecting dispersion and lifetime effects:

$$\rho_{e\text{-}pl}=\frac{3\pi^2\hbar^3}{\epsilon_0 m^2 k_F^2 v_s^2}\frac{q_m^4}{k\theta_1}\left(\frac{T}{\theta_1}\right)^3\frac{9\kappa_s^4}{\kappa_d^2}\int_0^{z_m}\frac{z^3dz}{(1-e^{-z})(e^z-1)}, \tag{4.1}$$

where $\kappa_{d,s}=4\pi e^2 N_{s,d}(E_F)$ and $z_m=\theta_1/T$. Including dispersion leads to a more complicated expression which has the factor $[1-(1-3N_s/N_d)(z^2/z_m^2)]^{-3}$ in the integrand of (4.1); Eq. (4.1) yields a $(T/\theta_1)^3$ dependence at low temperature and a linear dependence at high temperatures. The dispersion term will, in general, increase ρ and give higher powers of T. At $T=\theta_1\sim 35$ K and with parameters appropriate to Nb, Eq. (4.1) gives a value for ρ on the order 10^{-7} Ω cm. This is of the same order of magnitude as Webb[28] finds in his purest samples at these temperatures. Webb's data, however, scales with a Θ of ~270 rather than roughly 35°. Hence, while Eq. (4.1) would give a T^3 behavior in agreement with experiment at very low temperatures, i.e., $T\leq 0.3\theta_1$ it would not account for the observed T^3 behavior which dominates the resistivity up to room temperature. Lifetime effects, which produce a low wave number cutoff to the plasmon spectrum as well as reducing the maximum wave number, will change the temperature dependence of the resistivity since the limits in Eq. (4.1) will be temperature dependent. At high temperatures the acoustic plasmons cease to be elementary excitations and should not contribute to the resistivity in the same degree as Eq. (4.1) would indicate. For Nb_3Sn with its high residual resistivity[27] and high room-temperature resistivity, the lifetime effect is more important.

The anomalous resistivity of Nb_3Sn reported by Woodward and Cody[27] has been nicely fitted by Cohen, Cody, and Halloran[29] to a theory involving the rapid motion of the Fermi level as the temperature increases. On the basis of the Fröhlich model, one would expect the acoustic plasmons to dominate the scattering at low temperatures and the phonons at high temperatures. Indeed, the data is nearly linear from ~20—120 K and again from ~300—600°. The high-temperature region is characteristic of a θ of roughly 250 K, while the low-temperature region indicates a low value of θ on the order of ~50 K from the fact that it is linear already at ~30°. The region connecting the low and high linear portions and the absence of an acoustic plasmon contribution to the resistivity at high temperatures would be due to lifetime effects washing out the acoustic plasmon mode.

V. CRITERION FOR SUPERCONDUCTIVITY VIA ACOUSTIC PLASMONS

In the BCS theory and its extensions the criterion for superconductivity is essentially that an attractive interaction between electrons strong enough to overcome the repulsive Coulomb forces exist. Granted that such an interaction exists, a large density of states at the Fermi level should lead to high transition temperatures. In Fröhlich's model one deals with two densities of states, one for the s electrons and one for the d electrons. The ratio of these as shown in Eq. (2.10) determines whether an attractive interaction via the acoustic plasmons exists. In general, the usual electron-phonon interaction could lead to superconductivity in the absence of the plasmon mechanism. Hence, to test whether the plasmon mechanism is dominant we consider the transition metals and alloys and compare T_c and the density of states as determined from the electronic specific heat. The criterion given by Eq. (2.10) is

$$N_d(E_F)/3N_s(E_F)>1. \tag{5.1}$$

Using

$$\gamma_e=\gamma_d+\gamma_s\propto N_d(E_F)+N_s(E_F),$$

this condition becomes $\gamma_e>4\gamma_s$. There is some difficulty in determining what value γ_s should have. If we follow Gladstone, Jensen, and Schrieffer[25] and assume $N_s(E_F)=0.4$ (states/eV atom) for all transition metals, then $\gamma_s=0.945$ mJ/mole $(K)^2$. With this assumption our criterion for the existence of superconductivity via the acoustic plasmon mechanism is

$$\gamma_e>3.78\ \text{mJ/mole}\ (K)^2=\gamma_0. \tag{5.2}$$

Of the 23 nonmagnetic transition elements listed in Table I, 16 are superconducting. Of these, nine have $\gamma_e<\gamma_0$ and transition temperatures below 1.7 K. The remaining seven superconductors (including two phases of La) have T_c's above 4.4 K, except for Th, and $\gamma_e>\gamma_0$. The seven nonsuperconductors listed all have $\gamma_e>\gamma_0$. Of these, Y [30] and U [31] become superconducting under pressure, indicating that they are close to being intrinsic superconductors.

When (5.1) is well satisfied, one way that T_c can be small is for ϵ_0 to be very large. A large ϵ_0 decreases both F and $\omega_{p,m}$ and, hence, T_c can be quite sensitive to ϵ_0. We have shown in Sec. III that, from the specific-heat data for Nb and Nb_3Sn, $\gamma_F\sim 0.09$ and, hence, values of ϵ_0 on the order of 100 are indicated for these materials. Since ϵ_0 arises principally from interband transitions, we expect that it is given by an expression similar to the Phillips-Penn[32] expression for the dielectric constant. We can write

$$\epsilon_0\approx\omega_p^2/E^2, \tag{5.3}$$

TABLE I. Values of the electronic specific heat and transition temperature for nonmagnetic transition elements.

Element	$\gamma_e\left(\frac{mJ}{\text{mole (K)}^2}\right)$ [a]	T_c
W	1.22	0.012
Mo	2.10	0.92
Os	2.35	0.66
Hf	2.40	0.09
Re	2.40	1.70
Zr	2.91	0.52
Ir	3.15	0.10
Ru	3.30	0.51
Ti	3.41	0.39
Tc	4.06 [b]	7.77
Th	4.69	1.37
Ta	5.84	4.48
La(β)	6.70 [c]	6.06 [c]
Nb	7.80	9.22
V	9.80 [c]	5.38
La(α)	10.0 [c]	4.9 [c]
Rh	4.60	<0.01
Pt	6.68	<0.01
Pd	10.00	<0.01
U	10.9	?[d]
Sc	10.8	<0.01
Y	10.1	<0.03
Lu	10.22	<0.03

[a] Except where noted data are taken from Ref. 25, Table VI.

[b] Estimated.

[c] B. W. Roberts, Natl. Bur. Std. Technical Note No. 482, 1969 (unpublished).

[d] The filamentary superconductivity which exists at zero pressure is thought to be due to strains at grain boundaries.

where ω_p is the unscreened plasma frequency of the d electrons and E is an energy which is roughly the region of overlap of the d and s band near the Fermi level. We expect that E is on the order of the width of the d band or smaller. If a narrow d band partially overlaps the s band, then the transitions from s to d which contribute are those from filled s states for s electrons near the Fermi level to the unfilled part of the d band, and similarly for the d to s transitions. If a sharply peaked part of the d density of states lies at the Fermi level, $\epsilon_0(q_m)$ may be very large due to a small energy overlap, while $N_d(E_F)$ is still quite large. The assumption of narrow sharply peaked d states is common to most treatments of transition metals.[8,33]

In Table I the last seven elements listed are nonsuperconductors, not merely nonacoustic plasmon superconductors. Hence, the absence of the electron-phonon mechanism must also be explained. As we pointed out in the Introduction, the electron-phonon interaction can be viewed from the dielectric constant point of view[2,4,10]; thus a value of ϵ_0 large enough to suppress the acoustic plasmon interaction will also suppress the electron-phonon interaction.

From the above discussion and Table I we see that for the transition metal elements (5.1) is a necessary but not a sufficient condition that an element have a high T_c via the acoustic plasmon mechanism. For alloy systems the situation is quite similar.[34]

VI. PRESSURE DEPENDENCE OF TRANSITION TEMPERATURE

In the nontransition-metal superconductors, the transition temperature generally decreases with increasing pressure[35] (Tl at low pressures is an exception). This is in accord with the McMillan's[34] expression for T_c. For the transition metals, however, dT_c/dp has both positive and negative values.[35] This behavior is not well understood although various suggestions have been put forth.[35] In addition, it is known that Ba,[36] Ce,[37] Cs,[30] Y,[30] and U[31] become superconducting under high pressure, and independent studies of the resistivity of Ba under pressure[38] suggest that a d state is formed at the Fermi surface. Within the frame work of Fröhlich's model, both the pressure-induced superconductivity and the various signs of dT_c/dp in other transition metals are readily understood.

From (2.10) we note that in order for γ_F^2, and hence the interaction F, to be positive a minimum density of states in the d band is necessary. Hence, for Ba and Cs we expect no superconductivity until $N_d(E_F) > 3N_s(E_F)$. In this way the pressure-induced superconductivity results from a d state moving down to the Fermi surface with pressure or the s state moving up. The effect of pressure on the d character of the elements K to V and evidence for a s to d transition by shock waves, is discussed by Berggren.[39]

To treat the pressure dependence of T_c more generally we can differentiate (2.23), treating as independent variables $N_s(E_F)$, $N_d(E_F)$, ϵ_0, v_s, and v_d. Using (2.19), (2.23), and (2.9) one finds

$$\frac{1}{T_c}\frac{dT_c}{dp} = \frac{1+6\alpha/F}{2(1-3\alpha)N_d}\frac{\partial N_d(E_F)}{\partial p} - \frac{1}{2Fv_s}\frac{\partial v_s}{\partial p} - \frac{1}{\epsilon_0}\frac{\partial \epsilon_0}{\partial p}\left(\frac{1}{2}+\frac{1}{F}\right) + \left(1-\frac{1}{2F}\right)\frac{1}{v_d}\frac{\partial v_d}{\partial p} - \frac{3}{2(1-3\alpha)N_s}\frac{\partial N_s(E_F)}{\partial p}, \tag{6.1}$$

where $\alpha = N_s(E_F)/N_d(E_F)$. With so many parameters which can change with pressure, one could explain any variation of T_c with pressure. We shall show, however, that with reasonable assumptions some of the terms can be dropped from consideration. First, we consider the probable sign of the various terms. For the $N_d(E_F)$ term, except for Cs and Ba

where the d level may be just forming at the Fermi level, one expects pressure to broaden the d bands and decrease N_d. Hence, the N_d term will, depending on whether d state is just forming or is nearly filled, either increase or decrease T_c with increasing pressure. For the v_s and N_s terms, if we assume the s electrons behave as free electrons, N_s and v_s will increase with increasing pressure. Hence, these terms will tend to decrease T_c. For the v_d term one expects that under pressure the broadened d band would be more like a free electron gas, and hence v_d should increase with pressure. The sign of this contribution to dT_c/dp will, however, depend on whether F is greater or less than 0.5. For the ϵ_0 term we recall that it represents the contribution to the dielectric constand from band-to-band transitions and is expected to be given by (5.3). While ω_p will increase due to the increase of n_d with pressure, it is likely that E_d increases more rapidly; hence, we expect $\partial\epsilon_0/\partial p < 0$ and a positive contribution to dT_c/dp.

All the terms appearing in Eq. (6.1) may contribute dT_c/dp; the magnitude of the observed dT_c/dp, however, can be used as a guide to which terms are important. Table II contains some data on values of dT_c/dp for transition-metal elements and alloys. It is clear that the magnitude of dT_c/dp varies greatly in magnitude and is of both signs.

Our discussion of the criterion for superconductivity in Sec. V indicated that condition (5.1) was necessary but not sufficient for superconductivity. It thus appears that the $N_d(E_F)$ term is needed to explain the onset of superconductivity in Ba and Cs. For Ce, Y, and U, however, large $N_d(E_F)$ already exists and, hence, the change in overlap of the s-d band to which ϵ_0 is quite sensitive is the likely cause for superconductivity. The large dT_c/dp seen in La and Ba are also probably due to the ϵ_0 term.

For Nb, Mo, and Ta, we see small magnitudes of dT_c/dp and both signs. If this behavior is ascribed to the v_d term, then $F_{\mathrm{Nb}} > 0.5$, $F_{\mathrm{Ta}} < 0.5$, and $F_{\mathrm{Mo}} < 0.5$. For V and Zr with intermediate positive values of dT_c/dp, a variation in ϵ_0 may be involved.

While these assignments are not definitive, they do provide a way of sorting out the various complex experimental evidence in the transition metals.

TABLE II. Typical values of dT_c/d_p for various materials.

Substance	T_c(K)	dT_c/dp (K/kbar)[a]	Pressure range (kbar)
Ba	~1.4	$\sim 1\times10^{-4}$	55-75
Nb_3Sn	17.5	-2.1×10^{-4}	0-2
Nb_3Sn	17.5	-0.6×10^{-4}	25-30
La(hcp)	5.2	1.4×10^{-4}	0-20
V	5.1	1.8×10^{-5}	0-10
Nb	9.4	$\sim 7.5\times10^{-6}$	0-40
Ta	4.4	-2.6×10^{-6}	0-20
Zr	0.52	$\sim 1.4\times10^{-5}$	
Mo	0.92	$\sim -1.0\times10^{-6}$	

[a]Data is taken from Ref. 25, Table IX, and Ref. 35, Table II, except for Ba which is estimated from Ref. 36.

VII. MÖSSBAUER EFFECT AND LATTICE TRANSFORMATIONS

So far we have cited specific-heat anomalies, resistivity, density-of-states criterion, and the pressure dependence of T_c as possible evidence pointing to the reality of the acoustic plasmons. There are two other phenomena which may also be related: the anomalous Mössbauer data for Nb_3Sn,[40] and the lattice transformations in Nb_3Sn[41] and V_3Si.[42]

A. Mössbauer Effect

For Nb_3Sn, using Sn^{119}, Shier and Taylor[40] found that the Mössbauer recoil-free fraction was rather low and its temperature dependence not very strong. They interpreted their result in terms of highly anharmonic forces acting upon the tin atoms. When one considers what possible effect the acoustic plasmons could have, the following picture emerges. At low temperature the acoustic plasmons would be more highly excited than phonons, when they have a lower Debye temperature, and if the plasmons couple to the nuclear motion then they will reduce the recoil-free fraction f.

For a simple model of the lattice, Lipkin[43] writes

$$-\ln f = k^2 \langle x^2 \rangle_T = R(2n_T + 1)/\hbar\omega, \qquad (7.1)$$

where k is the wave number of the γ ray, $\langle x^2 \rangle_T$ is the thermal average square displacement of the emitting nucleus, R is the free recoil energy, n_T the Planck distribution for Bosons of energy $\hbar\omega$, and $\hbar\omega$ is the spacing of energy levels (and is loosely related to the Debye temperature). While (7.1) is more qualitative than quantitative, using $\hbar\omega = k\Theta$ and letting $T \to 0$ gives, with $R_{sn} = 2.6\times10^{-3}$ eV, $-\ln f = 30/\Theta$. The work of Shier and Taylor[40] gives $-\ln f = 0.8$, which would correspond to a Θ of roughly 37 K. This simply indicates that a low value of Θ is consistent with the low-temperature behavior of f. Our estimate of θ_1 for Nb_3Sn from specific heat was ~44 K.

Another approach which is again more qualitative than quantitative involves a comparison of the energy content of the acoustic plasmons and acoustic phonons as a function of temperature. If we assume that $\Theta_D = 5\theta_1$ and that there are three phonon modes for each q, as compared to one for the plasmons, we find that for $T \leq 1.55\theta_1$ the plasmons have more energy than the phonons. Hence, if the plasmons

couple to the nuclear motion they should dominate in the thermal average of $\langle x^2 \rangle_T$ at low temperatures.

The simplest interaction one could suppose for the interaction of the plasmons and the nuclear motion would be an electrostatic[44] one. Thus, the electric field of the plasmon acting on the nuclear charge would couple the nuclear motion to the plasmons. In metals which have only a single unfilled band, the plasma frequency is generally too high for the nuclear motion to follow the field. For the acoustic plasmons, however, this is not the case, and strong coupling could occur.

The general features of Fig. 2 of Shier and Taylor can thus be explained by acoustic plasmons determining the recoil-free fraction at low temperatures and the phonons determining it at high temperatures. The lessened influence of the plasmons at high temperatures can be understood in terms of the predominance of the phonons in the thermal energy at high temperatures or the lack of acoustic plasmons, due to lifetime effects at elevated temperatures.

The possibility of seeing similar effects in other materials is limited by the number of suitable nuclides, unless they are simply used as impurities. Among the elements, Ta^{181} may be a candidate.[45]

B. Lattice Transformation in Nb_3Sn (and V_3Si)

The existence of two or more excitation modes of the system in overlapping energy and wave-vector regimes suggests the possibility of strong interactions where their dispersion curves cross. We have already noted that the velocity of the acoustic plasmons should be in the range of sound velocities. The likelihood that the plasmons couple to the nuclear motion was mentioned in connection with the Mössbauer discussion. The only question remaining is what are the likely manifestations the interaction would have.

While one might expect in general that the plasmons being longitudinal excitations would couple more strongly to the longitudinal phonons, this is not necessarily so if the coupling is through the lattice displacements directly. (Anharmonic effects associated with the superposition of the displacement of the same nuclei by two excitations simultaneously should lead to coupling to all modes.) There is a possibility of a lattice transformation at low temperature induced by the presence of the acoustic plasmons, because as we have noted above, as the temperature is lowered there is a temperature below which the plasmons have more energy than the phonons. As this temperature is approached the plasmon modes play an increasingly important role in the thermal properties and dynamics of the system and may by a "forced oscillation" drive the lattice into a new mode of oscillation. It may not be coincidental that the estimated value of θ_1 from the specific heat of Nb_3Sn is ~44 K and Nb_3Sn exhibits a lattice transformation[41] at ~43 K. If we apply the same arguments to V_3Si, which has a lattice transformation[42] at ~22°, then a low θ_1 may be expected.

VIII. DISCUSSION

We have proposed that the acoustic plasmons, introduced by Fröhlich to explain the superconducting properties of some transition metals, have observable effects on the normal-state properties of these materials. The evidence cited for the existence of the acoustic plasmon consisted of various specific-heat anomalies, resistivity data, pressure-induced superconductivity and the variation of T_c with pressure, criteria for the occurrence of superconductivity, Mössbauer data, and lattice transformations. None of the data establishes the existence of the acoustic plasmons unambiguously. This treatment gives, however, a single approach which can explain consistently seemingly diverse phenomena.

The specific-heat data represent the strongest evidence for the acoustic plasmons. The fact that the anomalies are present in Nb and its alloys, as well as in Nb_3Sn and V_3Si, suggest that they are common to transition metals rather than to a particular crystal structure.

The occurrence of "high" T_c's and pressure-induced superconductivity also lend strong support for Fröhlich's model, with both satisfying (5.1). For the usual electron-phonon mechanism, no satisfactory explanation of the occurrence and pressure dependence of superconductivity in the transition metals exists.

The other cited properties, resistivity, Mössbauer results in Nb_3Sn, and lattice transformations, are indirect evidence for the proposed picture in that they can easily be fitted by the model. Other explanations, not in contradiction with the Fröhlich model, can, however, be applied to these effects.

Fröhlich has proposed[46] that neutron diffraction experiments might reveal the acoustic plasmons. Direct detection of an additional longitudinal acoustic mode might also be possible as long as $\omega\tau_d > 1$. For pure Nb[28] at low temperatures, $\tau_d \approx 5\times10^{-8}$ sec, while for Nb_3Sn,[27] $\tau_d \approx 2\times10^{-11}$ sec.

In many ways the Fröhlich model is identical to the phonon mechanism; indeed Fröhlich called the plasmons phonons. The physical parameters of the plasmon mechanism, however, are different from those of the phonon mechanism. The essential parameters are $N_d(E_F)$, v_d, and $\epsilon_0(q_m)$. When $N_d(E_F)$ is large, the parameter controlling T_c is $\epsilon_0(q_m)$, which is apparently sensitive to pressure and perhaps to other variables such as impurity content,

alloy composition, and crystallographic phase. It is the need for an understanding of the dependence of T_c on these parameters which makes a search for new mechanisms for superconductivity so important.

The purpose of any model is to explain previous unexplained phenomena and predict new results. The transition-element superconductors are one class of superconductors which have unexplained behavior. Recent work by Hopfield[47] has attempted to correlate some of the behavior using a "chemical" or atomic parameter η, which involves the p density of states and the electron-phonon interaction. Labbe *et al.*[48] have treated the transition metals by concentrating on the sharpness of the d density of states near the Fermi surface, but also utilizing the electron-phonon interaction. The Fröhlich model has features common to both of these, namely, the use of partial densities of state $N_s(E_F)$ and $N_d(E_F)$ and sensitivity to position of d level in $\epsilon_0(q_m)$, but does not utilize the electron-phonon interaction. In the Fröhlich model, $\epsilon_0(q_m)$ can depend critically on the sharpness of the d band through its overlap with the s band. The value of v_d which occurs in the expression for θ_1 and F can be viewed as a "chemical" property in the sense used by Hopfield.

This review of the Fröhlich model and its properties indicates that the acoustic plasmon mode exists and affects both the normal and superconducting properties of some transition elements and alloys. While the model has many features in common with the BCS theory[6] and theories particular to transition metals,[29,47,48] it is a nonphonon mechanism. The occurrence and pressure dependence of T_c in transition elements and elements such as Cs, Ba, Y, Ce, and U, which become superconducting under pressure, are readily explained by the model, whereas existing theories have had little success in these areas.[1,2] From existing specific-heat data, estimates of parameters entering the theory such as v_d and $\epsilon_0(q_m)$ can be obtained. Over-all, the model gives a satisfactory explanation for a number of diverse superconducting and normal properties of transition metals.

Further experimental work on the specific heat of elements such as La, Ta, and V[49] and compounds such as Nb_3Sn and V_3Si, in fields high enough to keep them normal at low temperatures, would be useful in testing the theory. A search for the acoustic plasmons by neutron diffraction, or other means, or independent determinations of v_d or $\epsilon_0(q_m)$ could also provide a test of the theory.

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[49]After this paper had been submitted, in reading the paper by R. Colella and B. W. Batterman [Phys. Rev. B 1, 3913 (1970)] we became aware of the work of G. A. Alers [Phys. Rev. 119, 1532 (1960)] in which the discrepancy between the Debye temperatures deduced from the elastic constants and the specific heat in V, led him to suggest that "the low-temperature specific heat includes a contribution which varies as T^3 in addition to the lattice T^3 term." The work of Colella and Batterman supports Alers' s hypothesis and, hence, V also appears to be a material in which acoustic plasmons are present. From the specific-heat Debye temperature and that deduced from elastic constants we can obtain a value for $f/\theta_1^3 \sim 8.5\times10^{-9}$ (K)^3. Since there appears to be no unambiguous data from which a value of $\Delta\gamma_e$ or a "break" temperature can be obtained, we have not evaluated the parameters for V. The need for specific-heat measurements on V over an extended range of temperatures, on the same sample, is also manifest in the work of J. A. Morrison and L. S. Salter [Phys. Letters 9, 110 (1964)], in which the uncertainties in comparing various data were pointed out.

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Correlation of the Superconducting Transition Temperature with an Empirical Pseudopotential Determined from Atomic Spectra

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We have observed a correlation between the superconducting transition temperature and the energy of the first excited electronic configuration of the atom as determined from the optical spectra. This has led to the formulation of an empirical pseudopotential using atomic spectral data. Using this pseudopotential we have shown it to be the dominant factor in accounting for the cohesive energy, melting temperature, Debye temperature, thermal expansion coefficient, and superconducting transition temperature.

Two rather distinct approaches to the study of superconductivity have evolved over the years. One approach has emphasized empirical correlations between superconductivity and a variety of other properties such as melting point, hardness, and position in the Periodic Table.[1] The other approach has attempted to explain superconductivity from first principles using simplified but still mathematically increasingly complex models.[2] These two viewpoints have on occasion complemented each other. For example, the observation that the tendency toward superconductivity is inversely related to the normal state conductivity provided one of the earliest clues that superconductivity arises from an electron-phonon interaction since a strong electron-phonon interaction is generally responsible for a low normal state conductivity.

On the other hand, the two approaches diverge