

## ELECTRON-PHONON INTERACTION AND CHARACTERISTICS OF METAL ELECTRONS

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## 1. INTRODUCTION

It was found in the last decade that the kinematics of the electrons of the metal in a magnetic field are determined by the topology of the Fermi surface<sup>[1]</sup>. This has uncovered ways of experimentally studying the Fermi surface of the conduction electrons. As a result, the Fermi surfaces of most metals are known by now (see the review<sup>[2]</sup>). It turned out that the Fermi surfaces of at least all the transition metals coincide, in first approximation, with the results obtained from calculations by the almost-free-electron model. In this model it is assumed that the conduction electrons behave like free ones, but owing to the periodic potential of the lattice they experience Bragg reflection from the boundaries of the Brillouin zone.

The calculation results can be fully reconciled with the experimental data only after taking into account the interaction between the electrons and the ion core. Inside the unit cell of the lattice one can usually separate the regions outside and inside the ion core. Outside the ion core, the potential energy is low and the wave function is smooth and close to a plane wave. Inside the ion core, on the other hand, the wave function oscillates rapidly, so that the kinetic energy cancels in part the potential energy of the core. To take these oscillations into account, it is convenient to use the wave functions of the internal shells. Accordingly, the wave functions of the electrons are expanded in plane waves orthogonalized with respect to the wave functions of the internal shells (the method of orthogonalized plane waves (OPW)).

For the OPW there appears in the Schrödinger equation of the smooth electron function, as a result of elimination of the oscillating part, a repulsion potential acting in the region of the ion core. This potential cancels to a considerable degree the initial attraction

potential. The resultant potential, customarily called pseudopotential, turns out to be weak enough to be treated by perturbation theory.

There exist several different methods of calculating the pseudopotential. Unfortunately, none are sufficiently reliable, so that the final results are corrected to fit metal parameters that depend on the choice of the pseudopotential. These characteristics may be the Fermi surface of the metal, the energies of the crystal and the band structures, the lattice vibration spectrum, etc. All these properties can be used to refine the pseudopotential parameters, which by now have been determined for a number of metals. Methods of calculating the pseudopotential are analyzed in detail in Harrison's monograph<sup>[3]</sup>.

It should be noted that the OPW and the pseudopotential concept can be used only in the case of strongly localized internal shells of electrons. This limits significantly the number of metals that can be successfully described by the OPW method. In particular, all transition metals are excluded from consideration.

When corrections are introduced for the action of the pseudopotential in the case of nontransition metals, it becomes possible to reconcile the results of the calculation of the Fermi surface with the experimental data. It turns out that allowance for the interaction does not affect strongly in this case the value of the Fermi energy, although the remaining characteristics of the electrons may be somewhat altered in comparison with the model of almost free electrons. In particular, for example, the effective mass of the electrons becomes somewhat altered, although in most metals this change does not exceed some 10%. The results of the calculations of the change of the effective mass of the electrons due to the interaction between the electrons and the ions are given in Table II below. The Heine-Abarenkov potential was used in the calculation<sup>[4]</sup> (see<sup>[3]</sup>).

We have assumed everywhere above that the ion cores are immobile. Actually, they can vibrate about an equilibrium position in the lattice. These lattice vibrations are described by using the phonon concept. The presence of an interaction between the electrons and the ion core causes the electron and phonon systems in the metal to be coupled to each other. There exists in a metal a noticeable electron-phonon interaction (EPI). This interaction plays an important role in the formation of the lattice-vibration spectrum; it alters considerably the connection between the energy and the momentum of the electrons near the Fermi surface; this interaction is responsible also for superconductivity. The present article is devoted to the consideration of different aspects of the EPI in metals. We first present briefly the results of a theoretical analysis of the problem, and then discuss the experimental data. The principal attention will be paid to the change produced by the EPI in the electron system. The role of the interaction between the electrons and the ions in the formation of the lattice-vibration spectrum will not be considered here. Those interested can find the corresponding data in Harrison's monograph<sup>[3]</sup> or in the paper of Brovman and Kagan<sup>[5]</sup>.

## 2. ELECTRON-PHONON INTERACTION PARAMETERS AND THEIR CALCULATION FOR A METAL IN THE NORMAL STATE

The calculation of the EPI reduces in final analysis to allowance for all the possible energy-exchange processes between the electron system and the phonons. Of course, in this case we deal with virtual phonons that can be excited in a solid. The general theory of this interaction is described in detail in a number of easily accessible monographs<sup>[6,7]</sup>; we present only a few of the most important conclusions. Thus, the EPI changes the electron energy and damping  $E_p$  and  $\Gamma_p$ . We note that the electrons are regarded as quasiparticles of the entire Fermi system:

$$E_p = E_p^0 + \text{Re } \Sigma(p, E_p + i\Gamma_p),$$

$$\Gamma_p = \text{Im } \Sigma(p, E_p + i\Gamma_p),$$

where  $p$  is the electron momentum and  $\Sigma$  is the irreducible self-energy part of the Green's function of the electrons, in which all the possible exchange methods are taken into account. The possibility of a fully correct calculation of  $\Sigma$  became obvious following publication of Migdal's 1958 paper<sup>[8]</sup>, where it was shown that the corrections to the zeroth term are of the order of smallness  $(m/M)^{1/2} \sim 10^{-2}$  ( $m$  and  $M$  are the masses of the electron and of the ion), and can therefore be neglected.

After calculating  $\Sigma$ , Migdal pointed out that  $\text{Re } \Sigma$  is proportional to  $\omega_p$  at small  $\omega_p$ , where  $\omega_p$  is the electron energy reckoned from the Fermi surface.

From this it followed directly that the EPI should change the state of the electrons near the Fermi surface, for example,

$$v_p = \partial E_p / \partial p = \partial E_p^0 / \partial p + (\partial \text{Re } \Sigma / \partial E_p) \partial E_p / \partial p,$$

$$v_p = v_{p, \text{band}} + (\partial \text{Re } \Sigma / \partial E) v_p,$$

or, denoting by  $\lambda = -\partial \text{Re } \Sigma / \partial E$  the average EPI parameter, we obtain

$$v_p = v_{\text{band}} / (1 + \lambda)$$

and accordingly

$$m = m_{\text{band}}(1 + \lambda), \quad N = N_{\text{band}}(1 + \lambda), \quad (1)$$

where  $v_{\text{band}}$ ,  $m_{\text{band}}$ , and  $N_{\text{band}}$  are the velocity, mass, and density of the electrons in the absence of the EPI, while  $v$ ,  $m$ , and  $N$  are the same quantities in the presence of EPI. One can speak of renormalization of the state of the electrons as a result of the EPI, if one introduces the renormalization coefficient

$$Z = 1 + \lambda;$$

then

$$v_p = v_{\text{band}} / Z, \quad m = m_{\text{band}} Z, \quad N = N_{\text{band}} Z.$$

Subsequent calculations by Prange and Kadanoff<sup>[9]</sup> have shown that the EPI does not change the Fermi energy, the anomalous skin effect, the spin-related magnetic susceptibility, all the galvanomagnetic-thermal coefficients, the electron mean free paths and the transport coefficients, the nuclear spin-lattice relaxation, and the frequency of the de Haas-Van Alphen effect.

It follows from (1) that the renormalization of the electron states as a result of the EPI is determined by the parameter  $\lambda$ . Obviously, in final analysis  $\lambda$  should be expressed in terms of the parameters of the electron-ion interaction and the lattice vibration spectrum of the metals<sup>[7]</sup>

$$\lambda = 2 \int g(\omega) \omega^{-1} d\omega, \quad (2)$$

where

$$g(\omega) = \sum_{\sigma} \int_S d^2 p \int_S d^2 p' \frac{|q_{pp'\sigma}|^2}{2\pi^3 v_F} \delta[\omega - \omega_{p-p',\sigma}] \int_S d^2 p, \quad (3)$$

$v_F$  is the velocity of the Fermi electrons. The integrals with respect to  $p$  and  $p'$  are taken over the Fermi surface  $S$ . They take into account all the possible electron transitions from the initial state  $|p\rangle$  to the final state  $|p'\rangle$ . These transitions are realized via excitation of the phonon field.  $q_{pp'\sigma}$  is the electron-phonon interaction constant, and  $\sigma$  is the polarization of the phonon-spectrum branches over which the summation is carried out. In the simplest case this is one longitudinal and two transverse branches. The phonon frequencies  $\omega_{p-p',\sigma}$  corresponds to the modes of the first Brillouin zone. With the aid of the pseudopotential method<sup>[10]</sup> it is possible to express  $q_{pp'\sigma}$  in terms of the form factor  $\langle p' | \mathfrak{B} | p \rangle$  of the scattering of the electrons from the state  $|p'\rangle$  into  $|p\rangle$  on the Fermi surface (see<sup>[3]</sup>):

$$q_{pp'\sigma}^2 = \frac{(p-p')^2 \epsilon^2(p-p') \langle p' | \mathfrak{B} | p \rangle^2}{2\omega_{p-p',\sigma} M N}, \quad (4)$$

where  $M$  is the mass of the ion,  $N$  is the number of ions per unit volume,  $\epsilon(p-p',\sigma)$  is the polarization vector corresponding to the phonon frequency  $\omega_{p-p',\sigma}$ .

All these expressions are simplified if one assumes a spherical Fermi surface and a local approximation for the pseudopotential<sup>[3]</sup>, in which  $\langle p' | \mathfrak{B} | p \rangle$  depends only on the change of the momentum  $q = p - p'$ ; then

$$g(\omega) = N^{-1} \sum_{\sigma} \int_{< 2k_F} (2\pi)^{-3} d^3 q L_{\sigma}(q) \delta[\omega - \omega_{q,\sigma}], \quad (5)$$

where

$$L_{\sigma}(q) = (m/4M) \frac{|\bar{q}_{\sigma}(q, \sigma)|^2}{k_F q \omega_{q, \sigma}} |\mathfrak{B}(q)|^2,$$

$\mathfrak{B}(q)$  is the local form factor of the pseudopotential, the integral  $d^3q$  is taken in a sphere of radius  $2k_F$ . Following<sup>[10-12]</sup>,  $g(\omega)$  is frequently represented in the literature in the form

$$g(\omega) = \alpha^2(\omega) F(\omega), \quad (6)$$

where

$$F(\omega) = N^{-1} \sum_{\sigma} \int (2\pi)^{-3} d^3q \delta[\omega - \omega_{q, \sigma}] \quad (7)$$

is the density of states of the lattice vibration spectrum.  $F(\omega)$  can be calculated, for example, from the dispersion curves for the lattice-vibration spectrum, which are determined usually by neutron diffraction.  $\alpha^2(\omega)$  is the EPI parameter, which can be determined by comparing the corresponding relations (5)–(7); such an expression for  $g(\omega)$  is convenient because it turns out that  $\alpha^2(\omega)$  varies more smoothly with energy than  $F(\omega)$ , and accordingly relation (6) emphasizes once more the change of  $g(\omega)$  is connected primarily with  $F(\omega)$ . As will be shown later on, the function  $g(\omega)$  can be determined from the experimental data.

As noted by McMillan<sup>[13]</sup>,  $\omega g(\omega)$  does not depend on the phonon energy (see relation (3)):

$$\int_0^{\infty} \omega g(\omega) d\omega = N_{\text{band}}^{\dagger} \hbar \langle g^2 \rangle / 2M,$$

where  $N_0$  is the density of the electrons on the Fermi surface,  $\langle g^2 \rangle$  is the square of the electron matrix element averaged over the Fermi surface. When relation (2) is used, we obtain for  $\lambda$  the approximate expression

$$\lambda = N_{\text{band}} \langle g^2 \rangle / M \langle \omega^2 \rangle, \quad (8)$$

where

$$\langle \omega^2 \rangle = \int \omega g(\omega) d\omega / \int g(\omega) \omega^{-1} d\omega.$$

By using the expressions (2)–(5) given above, we

Table I

Reference	Employed pseudopotential	Na	Al	Pb
14	Semiempirical	0.18	0.49	1.12
15	Heine-Animalu 1 OPW <sup>[3]</sup>	0.13	0.5	1.67
16	Heine-Animalu 2 OPW <sup>[3]</sup>	0.13	0.53	1.55
17	Heine-Animalu <sup>[3]</sup>	0.12	0.46	1.69
	Heine-Animalu <sup>[3]</sup>	0.15	0.53	1.34

can numerically calculate the averaged EPI parameter  $\lambda$ . One of the first numerical calculations of the averaged parameter was made by Ashcroft and Wilkins<sup>[14]</sup> for Na, Al, and Pb (Table I). They used a local pseudopotential in the calculation, and the integration was carried out over the Fermi surface altered by the electron-ion interaction. The calculation for these metals was subsequently repeated many times<sup>[15-17]</sup>. Although several different pseudopotentials were used, the values obtained for  $\lambda$  were all close (see Table I). The possible influence of the detailed form of the pseudopotential was verified also separately for lead in<sup>[18]</sup>.

The integration in the calculation of the averaged parameter  $\lambda$  causes all the quantities to be averaged. As a result, allowance for the anisotropy of the phonon spectrum seems to have no noticeable effect on the results in the case of metals with a cubic lattice. Thus, with sodium as an example<sup>[19]</sup>, it was shown that the maximum anisotropy of  $\lambda$ , due to the anisotropy of the lattice-vibration spectrum, does not exceed 2%.

Table II lists the values of  $\lambda$  calculated by Allen and Cohen for a number of nontransition metals. In<sup>[17]</sup>, a spherical model was used for most metals, both for the electrons and for the lattice vibrations. The pseudopotential used in the calculation is noted in Table II with the appropriate literature citation.

Table II

Metal	$T_c$ , °K	$\theta_D$ , °K	$\gamma$ , mJ/g-mole-°K	$\mu$	Pseudopotential in the calculation of $m_{\text{band}}$ and $\lambda^*$	Calculation of $m_{\text{band}}/m_0$	$\lambda$ (calculation of <sup>[16]</sup> )	$\lambda_c$ ** (calculation from (12); see below)	(calculation from (15); see below)	$\lambda_g$ and $\langle \omega \rangle$ , MeV	$\lambda_{cy}$
Na	—	157	1.8	1.26	Heine-Animalu	20	0.15 0.19	—	—	—	0.24 <sup>21</sup>
Mg	—	406	1.35	1.33	»	22	1.01 1.00 0.31	0.33	—	—	0.2–0.3 <sup>22</sup>
Be	0.026	1390 <sup>23</sup>	0.184	0.37	»	24	1.28 0.3 0.26	0.24	0.27	—	0.1–0.2 <sup>24</sup>
Cd	0.52	209 <sup>25</sup>	0.69	0.74	»	26	0.87 0.54 0.40	0.36	0.43	—	0.2–0.3 <sup>27</sup>
Zn	0.875	309	0.65	0.86	»	26	0.93 0.59 0.42	0.46	0.44	—	0.2–0.4 <sup>27</sup>
Ga	1.09	325 <sup>25</sup>	0.60	0.59	»	—	0.96 0.25	—	0.45	—	—
Al	1.2	420	1.36	1.47	»	35	1.04 0.97 0.52	0.47	0.44	—	0.4–0.8 <sup>28</sup> 0.5–0.6 <sup>29</sup> 0.6 <sup>31</sup>
Tl	2.39	78.5 <sup>32</sup>	1.47	1.10	»	—	0.82 0.55	1.07	0.63	0.78 (5)	0.4–0.8 <sup>33</sup>
In	3.40	109	1.80	1.44	»	30	0.89 0.74	0.6	0.81	0.83 (6.9)	0.6 <sup>34</sup> 0.5–0.7 <sup>30</sup>
Sn	3.72	202	1.82	1.30	»	37	0.93 0.73	0.56	0.66	0.72–0.78 (9.6)	0.6 <sup>36</sup>
Hg	4.15	72	2.0	—	»	39	0.8 0.89 0.98	—	1.10	1.6 (3.3)	0.75 <sup>38</sup> 1.2–1.4 <sup>40</sup>
Pb	7.2	94.5	3.0	2.0	»	41	0.86 1.34 1.32	1.33	1.32	1.5 (5.2)	1–1.4 <sup>41</sup>

\*In the case of two values of  $m_{\text{band}}/m_0$  for the Heine-Animalu potential, the upper value is calculated from [4] and the lower one from [17].

\*\*The arithmetic mean value of  $m_{\text{band}}/m_0$  was used in the calculation of  $\lambda_c$ .

Usually the calculation was carried out with a local potential. For metals with hexagonal structure, such as Be, Mg, Zn, and Cd, nonlocal potentials were also used<sup>[22,24,26]</sup>, which made it possible to describe more accurately the singularities of the Fermi surface of these metals. The results obtained with these pseudopotentials seemed to be more reliable. The Weiss pseudopotential<sup>[37]</sup> used to calculate the value of  $\lambda$  of tin, as follows from<sup>[42]</sup>, is apparently less accurate than the Heine-Abarenkov potential.

The errors in the obtained values of  $\lambda$  can probably reach 10–20%. They are connected with the leeway in the choice of the pseudopotential and with the approximations used to calculate the lattice vibration spectrum.

### 3. ELECTRON-PHONON INTERACTION AND SUPERCONDUCTIVITY OF METALS

We have considered the change of the states of the electrons of a normal metal. All these results actually have a limited region of applicability. The point is, as shown by Cooper<sup>[43]</sup> that the mutual attraction between the electrons gives rise to an electron bound state that is energywise more stable than a free electron gas. In this new state, the system of electrons is superconducting. Accordingly, all the results obtained for the normal state pertain either to the region above the temperature  $T_C$  of the transition into the superconducting state, or to fields stronger than the critical magnetic field of superconductors.

The theory of the onset of superconductivity is described in detail in the papers of Bardeen, Cooper, and Schrieffer<sup>[44]</sup> or Bogolyubov, Tolmachev, and Shirkov<sup>[45]</sup>. It was shown by them that the temperature of the transition to the superconducting state is

$$T_c \approx 0,7\Theta_D e^{-1/N_{\text{band}} W} \quad (9)$$

where  $\Theta_D$  is the Debye temperature and  $W$  is the potential of interaction between the electrons. We shall be interested only in the connection between the EPI parameters and the superconductor-pair binding energy  $\Delta$ .

The analysis of the EPI is made complicated in the case of superconductivity by the fact that the EPI in this case, unlike in the normal state, can no longer be regarded by perturbation theory. The reason is that the restructuring of the entire electron system as a result of the EPI has a qualitative character. Here, too, however, the problems become simplified if the method applied by A. B. Migdal to the normal state is used. With the aid of this method, Eliashberg<sup>[46]</sup> succeeded in finding a system of equations connecting the parameters of the electron-phonon interaction and  $\Delta(\omega)$ . Taking into account the Coulomb repulsion of the electrons, which was considered by Bogolyubov et al.<sup>[45]</sup> and later in<sup>[47]</sup>, these equations take the following integral form<sup>[7,11]</sup>:

$$\left. \begin{aligned} \Delta(\omega) &= \varphi(\omega)/Z(\omega), \quad \Delta(\Delta_0) = \Delta_0, \\ \varphi(\omega) &= \int_{\Delta_0}^{\omega_c} \text{Re} \frac{\Delta(\omega') d\omega'}{[\omega'^2 - \Delta(\omega')^2]^{1/2}} \int g(\omega') O^+(\omega'', \omega', \omega) d\omega'' - U_C(\omega_c), \\ Z(\omega) &= 1 - \omega^{-1} \int_{\Delta_0}^{\omega_c} \text{Re} \frac{|\omega''| d\omega''}{[\omega''^2 - \Delta(\omega'')^2]^{1/2}} \int g(\omega') O^-(\omega'', \omega', \omega) d\omega'', \end{aligned} \right\} (10)$$

where

$$O^\pm = \frac{1}{\omega'' + \omega' + \omega + i\delta} \pm \frac{1}{\omega'' + \omega' - \omega - i\delta} \quad (\delta \rightarrow 0),$$

$U_C(\omega)$  is the Coulomb potential introduced in<sup>[47]</sup>:

$$U_C(\omega) = N_{\text{band}} V_C [1 + N_{\text{band}} V_C \ln(E_F/\omega_c)]^{-1}, \quad U_C(\omega_e) \equiv u^*, \quad (11)$$

where  $V_C$  is the Coulomb interaction averaged over the Fermi surface, and  $\omega_e$  is the end point of the lattice vibration spectrum.

If we compare relations (1), (2), and (10), we can easily see that the changes of the electron system in the normal and superconducting states actually define one and the same function  $g(\omega)$ .

The system of integral equations (10) can be solved with respect to  $\Delta_0$  or  $T_C$ , the parameters of the lattice-vibration spectrum and the EPI, under certain simplifications. The best-known at present is the solution of McMillan<sup>[13]</sup>, who determined numerically an expression for  $T_C$ . He replaced  $g(\omega)$  in the calculation by the function  $F(\omega)$  determined for niobium by neutron diffraction. For the simplified calculation, McMillan assumed that  $g(\omega') \equiv 0$  at  $\omega' < 10$  MeV;  $\omega_e = 30$  MeV.

Under these assumptions,

$$T_c = (\Theta_D/1.45) \exp \left[ -\frac{1.04(1+\lambda)}{\lambda - u^*(1+0.62\lambda)} \right], \quad (12)$$

or

$$T_c = \langle \omega \rangle / 1.20 \exp \left[ -\frac{1.04(1+\lambda)}{\lambda - u^*(1+0.62\lambda)} \right], \quad (13)$$

where

$$\langle \omega \rangle = \int g(\omega) d\omega / \int g(\omega) \omega^{-1} d\omega. \quad (14)$$

Approximate expressions for  $T_C$  of superconductors were obtained also by Garland et al.<sup>[48]</sup> and by Geilikman<sup>[49]</sup>. These expressions, as well as relation (12), are not absolutely exact, but they are perfectly suitable for an estimate of the parameters. Table II lists the values of  $\lambda T_C$  calculated from  $T_C$ ,  $\Theta_D$ , and McMillan's relation (12). It was assumed in the calculation that  $u^* = 0.13$  for all metals, and the values of  $\Theta_D$  are given in Table II.

As is well known, the lattice-atom vibration frequency and  $\Theta_D$  are proportional to  $M^{-1/2}$ , where  $M$  is the mass of the atom. This makes it possible to verify, using samples with different isotopic compositions, the degree to which relations (9)–(12) actually describe the change of the critical temperature of the samples. Table III gives the results of an investigation of the isotopic effect in different superconducting metals, namely the values of  $\beta$  determined from the  $T_C \sim M^{-\beta}$  relation (the values of  $\beta$  were taken from the review<sup>[51]</sup>). According to the BCS theory [Eq. (9)] one should expect  $\beta = 0.5$ , and it was assumed for some time that only this value could obtain in metals in the case of superconductivity due only to the EPI. Actually, however,  $\beta$  is smaller than this value for a number of metals.

The decrease of  $\beta$  was explained by Morel and Anderson<sup>[47]</sup>, who pointed out that the dependence of  $u^*$  on  $\Theta_D$  should change the connection between  $T_C$  and  $M$ . As follows from (8), for example,  $\lambda$  should not change when the mass of the atom changes. The influence of  $u^*$  on the isotopic effect can be easily traced

Table III

Metal	$\beta_{\text{exp}}$	$\beta_{\text{calc}}^{47}$	$\beta_{\text{calc}}^{50}$	$u^*$	Metal	$\beta_{\text{exp}}$	$\beta_{\text{calc}}^{47}$	$\beta_{\text{calc}}^{50}$	$u^*$
Pb	$0.48 \pm 0.01$	0.47	$0.485 \pm 0.005$	—	Mo	$0.33 \pm 0.05$	0.3	$0.35 \pm 0.075$	0.1
Hg	$0.5 \pm 0.03$	0.46	$0.48 \pm 0.005$	—	Re	$0.39 \pm 0.01$	0.41	$0.355 \pm 0.005$	0.1
Sn	$0.47 \pm 0.002$	0.42	$0.455 \pm 0.01$	—	Os	$0.20 \pm 0.05$	0.25	$0.225 \pm 0.1$	0.12
Tl	$0.5 \pm 0.1$	—	$0.48 \pm 0.02$	—	Zr	0.0	0.30	$0.15 \pm 0.17$	0.17
Cd	$0.5 \pm 0.1$	0.34	$0.385 \pm 0.025$	—	Cu	$0.0 \pm 0.1$	0.35	$0.065 \pm 0.15$	0.15
Zn	$0.3 \pm 0.01$	0.35	$0.415 \pm 0.015$	0.12					

by using (12), from which we obtain

$$\beta = \frac{1}{2} - \frac{1}{2} \left( u^* \ln \frac{\Theta_D}{1.45T_c} \right)^2 \frac{1+0.62\lambda}{1+\lambda}.$$

Table III lists the values of  $\beta$  calculated by Morel and Anderson<sup>[47]</sup> and by Garland<sup>[50]</sup>. The calculated values of  $\beta$  are close to the experimental ones.

Thus, the deviation of the isotopic effect from the predictions of the simplest BCS theory still cannot serve as a basis for stating that the superconductivity in a given metal is connected with a nonphonon mechanism. Allowance for the Coulomb repulsion explains the deviation of  $\beta$  from 0.5.

We can use an inverse procedure and calculate the value of  $u^*$  from  $\beta$  and  $T_c/\Theta_D$  under the assumption that  $\lambda < 1$ , in accordance with the relation

$$u^* = (1 - 2\beta)^{1/2} [\ln(\Theta_D/1.45T_c)]^{-1}.$$

The values obtained in this manner for a number of metals were given in Table III. They do not contradict the value  $u^* = 0.13$  assumed in the calculation of  $\lambda T_{C^*}$ .

The values of  $\lambda T_{C^*}$  determined with the aid of (12) are not very accurate. The error in  $\lambda T_{C^*}$  can reach 10–15%; the error is particularly large for metals with a large ratio  $T_c/\Theta_D$ , since  $F(\omega)$  and  $g(\omega)$  for these metals extend to the low-energy region. More reliable results will be obtained, of course, by calculating  $\lambda$  directly from the experimentally determined function  $g(\omega)$ .

#### 4. EXPERIMENTAL DETERMINATION OF THE FUNCTION $g(\omega)$

The possibility of determining  $g(\omega)$  from tunnel characteristics of superconductors is connected with the 1962 paper of Giaever et al.<sup>[52]</sup>. By measuring the characteristics of a tunnel junction with lead at  $T < 1^\circ\text{K}$ , the authors observed a distinct deviation from the predictions of the BCS theory at an energy on the order of the Debye energy of lead. According to this theory (see also<sup>[7,11]</sup>), the current through a tunnel junction consisting of a normal metal and a superconductor is equal at  $T = 0$  to

$$I_{sn} = c \int_0^V N_s(\omega) d\omega, \quad N_s = N_n \operatorname{Re} \left[ \frac{|\omega|}{(\omega^2 - \Delta^2)^{1/2}} \right], \quad (15)$$

where  $c$  is the transparency of the barrier and  $\Delta$  is the width of the gap in the superconductor electron spectrum.

Giaever's results were subsequently repeated and obtained in a more district form<sup>[53]</sup>. In these and all the subsequent studies, a modulation procedure was used to measure  $dI/dV$ . As seen from (15),

$$R(V) = \frac{dI_{sn}/dV}{dI_{nn}/dV} = \frac{N_s}{N_n} = \operatorname{Re} \frac{|\omega|}{(\omega^2 - \Delta^2)^{1/2}} \approx 1 + (2\omega^2)^{-1} \operatorname{Re} \Delta^2. \quad (16)$$

The dashed line in Fig. 1 shows the prediction of the BCS theory, according to which  $\Delta$  is independent of  $\omega$ , while the solid line shows the experimental results. At 4, 5, and 9 MeV one can see an appreciable disparity between the predictions of the theory and experiment. The nature of these deviations can be understood on the basis of Eliashberg's equations (10). Unlike the BCS equations, they made it possible to determine the change of  $\Delta$  with changing energy  $\omega$  when  $\omega > \Delta_0$ , and to connect this change with other parameters of the metal. Thus, Scalapino and Anderson<sup>[10]</sup> found that although  $\Delta(\omega)$  and  $F(\omega)$  are connected by a system of integral equations, all the main features of the phonon density of states  $F(\omega)$  should appear in the  $\Delta(\omega)$  dependence, and by the same token in the tunnel characteristics. Finally, Schrieffer et al.<sup>[11]</sup> have shown how by properly choosing the function  $g(\omega)$  it is possible to describe qualitatively the experimental results using (10) and (16).

Further progress in this direction was made by McMillan and Rowell<sup>[54]</sup>, who showed that the experimentally determined function  $R(V)_{\text{exp}}$  can be used to determine numerically the function  $g(\omega)$ .  $g(\omega)$  was calculated by a successive-approximation method, during the course of which  $R(V)_{\text{exp}}^{g_e(\omega)}$  calculated from relations (10), (16), and  $g_e(\omega)$  is compared with the experimental function  $R(V)_{\text{exp}}$ . The calculation continues until  $R(V)_{\text{calc}}^{g_e(\omega)}$  and  $R(V)_{\text{exp}}$  are completely reconciled. During each state of the iteration of  $g(\omega)$ , the Coulomb potential  $u^*$  is chosen such as to make the calculated  $\Delta_0 = \Delta(\Delta_0)$  coincide with the experimental value.

The results of the reconstruction of  $g(\omega)$  of lead in accordance with the data of McMillan and Rowell are shown in Fig. 2. When  $g(\omega)$  is compared with the pho-

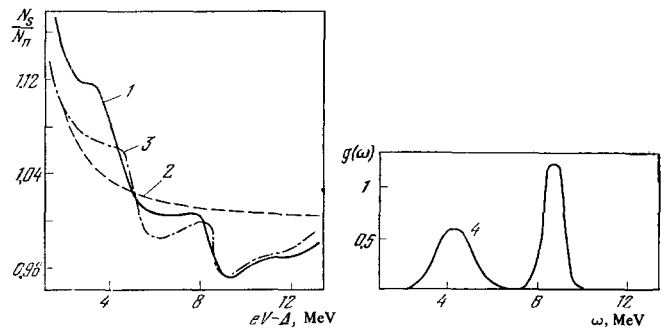


FIG. 1. Energy dependence of the relative density of states of the electrons  $N_s/N_n$  of lead in the superconducting state. 1—Experimental data obtained from tunnel measurements; 2—calculation by the BCS theory; 3—calculations<sup>[11]</sup> from Eliashberg's equations (10) with  $g(\omega)$  represented by curve 4.

non density of states  $F(\omega)$  calculated from the measurements of Brockhouse<sup>[59]</sup>, it turns out that these curves differ strongly both in position and in the type of principal maximum. This discrepancy could not be attributed to  $\alpha^2(\omega)$ , which changes little with changing energy, and its causes were not understood until 1967, when the neutron-diffraction measurements of the dispersion curves of lead were repeated<sup>[57]</sup>. Then, unlike in the preceding experiments, the measurements were performed also for many asymmetrical directions of the crystal lattice. These results were used for new calculations of the phonon density of states<sup>[56]</sup>. It turned out that the corrected value of  $F(\omega)$  agrees better with  $g(\omega)$  (see Fig. 2). Some systematic difference between the positions of the maxima is possibly connected with the difference between the temperatures of the tunnel and neutron-diffraction measurements. All these measurements dispelled whatever doubts there were concerning the possibility of reconstructing the function  $g(\omega)$ , which describes the EPI in a metal, from the tunnel characteristics.

Lead is one of the metals having the strongest EPI. Therefore the singularities of its tunnel characteristics are still strongly pronounced. In other superconductors they are not so large, and their measurement calls for a more sensitive procedure, say the measurement of  $d^2I/dV^2$  in addition to  $dI/dV$ .

By now, singularities of  $g(\omega)$  were observed in the tunnel characteristics of most investigated superconductors: Al<sup>58</sup>, Tl<sup>59-61</sup>, In<sup>54,59-62</sup>, Sn<sup>54,59</sup>, Hg<sup>63</sup>, Ta<sup>64,65</sup>, La<sup>66</sup>, Nb<sup>64</sup>, and a number of alloys.

In the case of metals with a very simple lattice, three singularities usually appear, and are connected with the transverse and longitudinal oscillation modes, and also with the end point of the spectrum. Metals having several atoms per unit cell (Sn, Hg) exhibit also optical modes. The number of singularities on the tunnel characteristics is large in this case; in the case of tin, for example, there are seven of them (see Fig. 6 of<sup>[67]</sup>) and it is difficult to identify all of them, all the more since the dispersion curves are usually determined for symmetrical directions. But this, as seen with lead as an example, is not sufficient to determine the exact form of  $F(\omega)$ .

The function  $g(\omega)$  was completely reconstructed for a number of metals. It is shown in Figs. 2-4. For tin, the figure shows in addition to the  $g(\omega)$  curve also the results of neutron-diffraction measurements of  $F(\omega)$  by Kotov et al.<sup>[68]</sup>. The dispersion curves for Sn were measured by Rowell<sup>[69]</sup>. The agreement between the measured  $g(\omega)$  and the neutron-diffraction data is perfectly satisfactory if the low accuracy of the latter is taken into account.

Recently Rowell and Dynes<sup>[70]</sup>, comparing all the known tunnel and neutron-diffraction data on the lattice-vibration spectrum, reached the conclusion that they are in satisfactory agreement.

The functions  $g(\omega)$  obtained from an analysis of the measurements of the tunnel effect can be used to calculate the parameter  $\lambda$  (see relation (2)). The obtained values of  $\lambda_g$  are listed in Table II. This is apparently the most consistent method of determining the EPI from the superconducting characteristics. The possible error in the presented values of  $\lambda_g$  is probably not

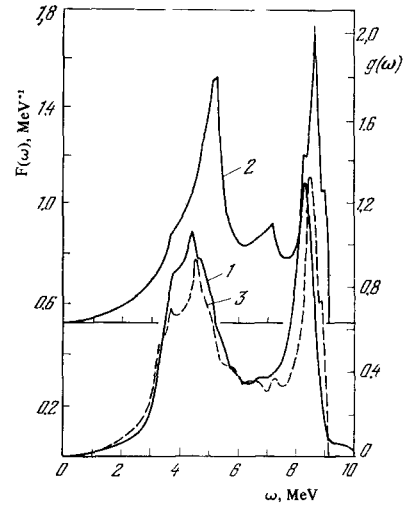


FIG. 2. Comparison of  $g(\omega)$  of lead, reconstructed from tunnel measurements in accordance with the data of [54] (1), with the phonon density of states  $F(\omega)$  determined by Brockhouse et al. [55] from an analysis of neutron-diffraction measurement only along the symmetry directions (2), and the data of Stedman et al. [56] (3), in which asymmetrical directions were also taken into account.

more than 3-4% in the case of Hg and Pb. The results of the calculations of  $\lambda_g$  known to us lie within the same limits, with the exception of the first 1965 paper by McMillan and Rowell<sup>[54]</sup> ( $\lambda_g = 1.33$ ). For the remaining metals, the possible error in the presented values of  $\lambda_g$  may probably reach 10-15%. This is connected both with the smaller amplitude of all the singularities due to  $g(\omega)$  and with the strong influence of the Coulomb potential  $u^*$  on the results of the reconstruction of  $g(\omega)$ . The program employed to reconstruct  $g(\omega)$  leads to noticeable differences in  $\lambda_g$ , depending on the choice of  $u^*$ .

## 5. DETERMINATION OF THE PARAMETERS OF THE ELECTRON-PHONON INTERACTION FROM THE CHARACTERISTICS OF THE METAL IN THE NORMAL STATE

As already indicated, the EPI leads to a change in the electron density, the effective mass, and the electron velocity near the Fermi surface. Obviously, measurement of all these quantities can yield the EPI parameters (see (1)).

a) Specific heat. It is known from the electron theory of metals that at low temperatures the specific heat of free electrons  $C_e$  is equal to

$$C_e = (4\pi^2 m k^2 / 3h^2) v_m (3n/\pi)^{1/3} T, \quad (17)$$

where  $k$  is Boltzmann's constant,  $n$  is the number of electrons per unit volume, and  $m$  is the electron mass. After substituting the numerical values we have

$$C_e = 0.136 \mu v_m^{2/3} n_a^{1/3} T \text{ mJ/g-mole} = \gamma T,$$

where  $v_m$  is the molar volume,  $n_a$  is the number of conduction electrons per atom,  $\mu = m/m_0$  and  $m_0$  is the mass of the free electron. From (17) we obtain

$$\mu = m/m_0 = 7.3 (n_a v_m^2)^{-1/3} \gamma. \quad (18)$$

The specific heats of metals at low temperatures have been measured quite reliably by now. Table II

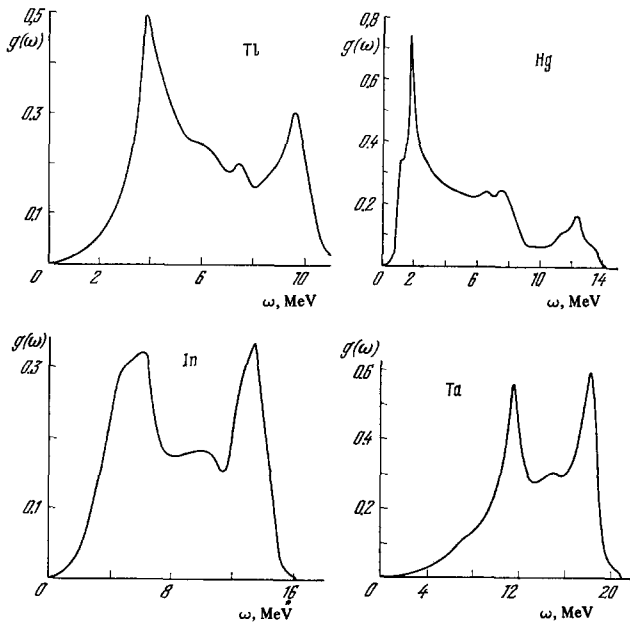


FIG. 3. The function  $g(\omega)$  for Tl [61], Hg [63b], In [54], and Ta [65], reconstructed from the tunnel characteristics.

lists the values of  $\Theta D$  and  $\gamma$ , which are the coefficients in the linear term of the specific heat. For most metals, the values were taken from the review [71]. For certain metals, Table II gives more accurate data that agree with the latest publications listed in the bibliography.

From the values of  $\gamma$  for metals one can calculate with the aid of (18) the effective mass of the conduction electrons. For most metals, it differs from the free-electron mass. This difference may be connected, first, with a certain deformation of the Fermi surface by virtue of the electron-ion interaction. Second, the density of the electrons may be altered by the electron-electron and electron-phonon interactions.

The influence of the deformation of the Fermi surface can be calculated by using the known pseudopotentials of the metals. The obtained values of  $m_{\text{band}}/m_0$  are listed in Table II. The electron-electron interaction usually causes insignificant changes in the mass, and will be neglected. The deviation of  $m/m_{\text{band}}$  from unity will be attributed mainly to the EPI. We can then calculate from the measured values of the specific heat  $C_e$

$$\lambda_c = (m_e/m_{\text{band}}) - 1. \quad (19)$$

The values obtained in this manner are listed in Table II.

b) Cyclotron mass. As is well known, in a magnetic field the electron moves in a momentum-space plane perpendicular to the direction of the field  $H$ . For free electrons, the frequency of revolution around the field is

$$\omega_{\text{cy}} = eH/m_{\text{cy}}c, \quad (20)$$

where  $c$  is the speed of light. Such a periodic motion is experienced in the metal also by the conduction electrons. The frequency of revolution of the electrons (the cyclotron frequency) can be determined from the high-frequency resistance of the metal [10]. In this

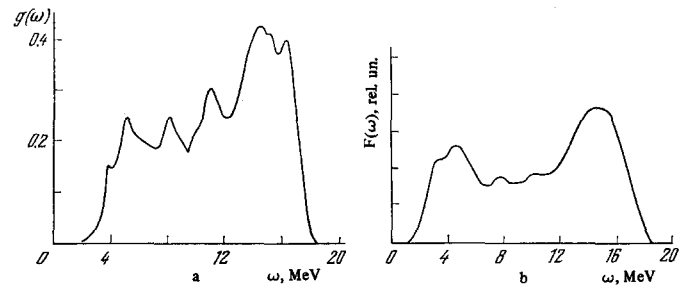


FIG. 4. The function  $g(\omega)$  for Sn, reconstructed from the tunnel characteristics by McMillan [54] (a), and  $F(\omega)$  determined by neutron diffraction by Kotov et al. [68] (b).

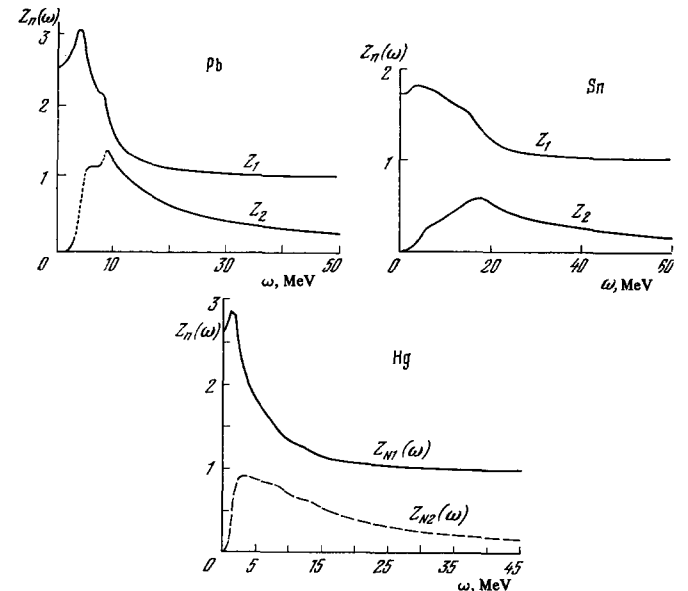


FIG. 5. Energy dependence of the renormalization coefficient  $Z_n$  in the normal state for Pb [54], Sn [54], and Hg [63].  $Z_1$  and  $Z_2$  are the real and imaginary parts of the renormalization coefficient.

case, however, the electron mass differs significantly from the mass of the free electron. Moreover, one usually observes several masses, the values of which change in a complicated manner when the sample orientation is changed. The reason for it is that in a metal the electron moves on the Fermi surface along a trajectory that is strictly specified by the experimental conditions. Accordingly, the role of the mass in (20) is played by

$$m_{\text{band cy}} = (2\pi)^{-1} dS/d\omega, \quad (21)$$

where  $S$  is the extremal area of the orbit in momentum space and  $\omega$  is the energy. Obviously,  $m_{\text{band}} = m_0$  for free electrons only in the case of a sphere. For each experiment, using (21), the influence of the shape of the trajectory, and the  $m_{\text{band cy}}$  obtained in this manner can be compared with the cyclotron mass calculated from (20).

Another way of determining the electron mass is to measure the temperature dependence of the amplitude of the de Haas-van Alphen effect. The accuracy of this method is however not as high as that of the cyclotron-resonance method.

The results of such a comparison shows that although allowance for the influence of the shape of the trajectory does indeed explain both the presence of several masses and the unisotropy of the cyclotron mass, nevertheless  $m_{cy}$  turns out to be systematically larger than  $m_{band,cy}$ . This difference, just as in the case of the specific heat of a metal, can be attributed to the EPI and the parameter  $\lambda$  can be determined by one more method, using a relation similar to (9). The values of  $\lambda_{cy}$  obtained in this manner are listed in Table II.

The accuracy with which the parameter  $\lambda$  is determined in this case is determined primarily by the reliability of the calculation of  $m_{band,cy}$ . The error in the experimental measurement of  $m_{cy}$  usually does not exceed a fraction of 1%, which is much smaller than the uncertainty in the value of  $m_{band,cy}$ . For example,  $m_{band,cy}$  for tin was calculated<sup>[36]</sup> using the model of almost free electrons; as a result, the values of  $\lambda_{cy}$  listed in Table II are apparently underestimated.

For a number of metals, Table II gives several values of  $\lambda_{cy}$ . The reason is that usually the ratio  $m_{cy}/m_{band,cy}$  depends on the Fermi-surface trajectory for which it is determined. Obviously, this is connected with the appearance of anisotropy of the EPI. In this case, unlike the specific heat, the averaging of the EPI parameters is only along the experimentally specified trajectory on the Fermi surface.

In a comparison of the results of the calculation with experiment it was noted that very frequently  $m_{cy}/m_{band,cy}$  differs systematically for electron trajectories passing through different bands of the Fermi surface. Thus, calculation of the experimental data of Khaikin and Mina for lead<sup>[72]</sup> and indium<sup>[34]</sup> has shown that in the case of lead  $(m_{cy}/m_{band,cy})_4 = 2.0$  for all electron trajectories pertaining to the fourth hole band, and  $(m_{cy}/m_{band,cy})_5 = 2.2-2.4$  for the trajectories of the fifth electron band. In the case of indium,  $(m_{cy}/m_{band,cy})_2 = 1.48-1.53$  and  $(m_{cy}/m_{band,cy})_3 = 1.6-1.7$  for the trajectories of the second and third bands, respectively. For thallium in the third and fourth bands,  $(m_{cy}/m_{band,cy})_3 \approx 1.4$  and  $(m_{cy}/m_{band,cy})_4 \approx 1.8$ . Such a systematic discrepancy is observed only when the calculations are based on the measurement of the cyclotron mass, and it is difficult to assume that it is connected with errors in the calculation of the Fermi-surface parameters. The EPI parameter  $\lambda$  of these metals probably differs by 20-30% for different bands of the Fermi surface.

Such data can be of undisputed interest for the understanding of the nature of the anisotropy of the energy gap of superconductors. The point is that the author has previously observed<sup>[73]</sup> in tin a relation between the size of the gap and the band whose electrons make the main contribution to the tunnel current. Subsequently such results were obtained also for gallium<sup>[74]</sup> and lead<sup>[75]</sup>. It would be very desirable to compare the EPI parameters of different bands, determined in the normal state, with the anisotropy of the gap in the superconducting phase. Of course, one cannot expect to be able to calculate directly the anisotropy of  $\Delta$  from the anisotropy of the parameters of the EPI of the normal phase, since superconductivity is a typically collective effect, but a correlation be-

tween these quantities is quite probable. This problem has not yet been dealt with adequately either experimentally or theoretically. For example, Eliashberg's cited system of equations (10) for the gap was obtained only for an isotropic metal.

Results on the gap anisotropy of Pb<sup>75</sup>, Ga<sup>76</sup>, Nb<sup>77</sup>, and Re<sup>78</sup>, measured by the tunnel-effect method, were published recently. In the case of transition metals (Nb and Re), no direct connection was established in these papers between the anisotropy of the gap and the structure of the Fermi surface. From among the latest calculations of the gap anisotropy, we note the calculations of the anisotropy of Al by Dynes and Carbotte<sup>[79]</sup>.

We have considered a number of ways of determining the EPI parameters for metals. As seen from Table II, all lead to values that agree within 10-20%. Only in individual cases are larger discrepancies in the values of  $\lambda$  observed, probably due to errors in the calculations, for example the approximate character of relations (12), errors in the calculation of  $m_{band}$ , etc. Of all the considered methods, the most reliable at present is the determination of the EPI parameters directly from  $g(\omega)$ , although this method is applicable to a limited number of superconductors. The greatest accuracy can be obtained in measurements of  $\lambda_{cy}$ , although additional calculations are needed here, and their accuracy is low. So far, apparently, we can determine the values of  $\lambda$  only with an error reaching 10%.

It would be very desirable to determine the EPI by a direct method requiring no additional calculations. To this end we must examine, first, how the EPI varies when the state or the parameters of the system of electrons and phonons is altered.

## 6. DEPENDENCE OF THE ELECTRON-PHONON INTERACTION ON THE ELECTRON ENERGY

As already indicated, all the expressions considered above pertain to the limiting case  $T = 0$ , or, more accurately,  $\omega \ll \omega_q$ , where  $\omega$  and  $\omega_q$  are the electron and phonon energies. Usually the energy of the Fermi electrons is many times larger than the phonon energy. Consequently, if we stay within the framework of the Fermi-system concepts, we can regard the EPI also outside the indicated limitation  $\omega \ll \omega_q$ . We can separate three different regions<sup>[8]</sup>:  $\omega < \omega_q$ ,  $\omega \sim \omega_q$ , and  $\omega > \omega_q$ . The results pertaining to the first region were already considered; EPI causes here a renormalization of most characteristics of the electron state. In the second region, energy exchange between the electron and phonon systems increases to such an extent that the quasiparticle damping coefficient turns out to be of the order of their energy. Obviously, under these conditions the very concept of electron as a quasiparticle becomes meaningless. Finally, in the region  $\omega > \omega_q$  all the effects connected with the EPI vanish gradually.

Figure 5 shows the calculated energy dependence of the renormalization coefficient  $Z_n$  for lead, mercury and tin. The calculations were made using the  $g(\omega)$  shown in Figs. 2-4, and were based on relation (10) for  $Z$ , in which  $\Delta(\omega) \equiv 0$  was assumed. One sees



both a sharp increase of the imaginary part of  $Z_n$  at  $\omega \sim \omega_q$ , characterizing the damping of the quasiparticles, and a gradual decrease of the role of the EPI with increasing energy,  $Z(\omega) \rightarrow 1$  as  $\omega \rightarrow \infty$ .

From the dependence of the characteristics of the metal on the energy one could determine directly the renormalization parameter  $Z_0$  and by the same token the EPI. Such experiments are at present still in the initial stage.

From among similar experiments, we consider first the experiments aimed to determine the energy dependence of the cyclotron mass. In these experiments, the average electron energy was increased by increasing the sample temperature. The most thoroughly investigated were the changes of the cyclotron mass of lead [80,81] and zinc [82]. In both metals, an increase of the cyclotron mass was observed when the temperature was raised from 1 to 7–10°K (in the case of lead  $m_{CY}(T) = m_{CY,0}(1 + 1.07 \times 10^{-3}T^2)$ ). This effect turned out to be in good agreement with the results of theoretical estimates of the possible EPI-induced increase of the mass [83]. At this stage these experiments, besides confirming the role of the EPI, uncover a possibility of verifying by one more method the character of the variation of  $g(\omega)$  of the investigated metals as  $\omega \rightarrow 0$ . The results obtained in the case of Pb and Zn show that  $g(\omega) \sim \omega^n$ , where  $n \geq 2$ , as  $\omega \rightarrow 0$ .

All the experiments revealed also a strong broadening of the cyclotron-resonance line with increasing temperature, thus indicating a decrease in the quasiparticle lifetime  $\tau$ . For example, in the case of lead  $\tau^{-1} = \tau_0^{-1} + aT^{3 \pm 0.3}$ , where  $\tau_0 = (0.7^{80} = 1.2^{81}) \cdot 10^{-9}$  sec and  $a = (1.72^{80} - 1^{81}) \cdot 10^{-8}$  sec $\cdot$ °K $^{-3}$ . This effect is connected with the increase of the imaginary part of  $Z_n$  with increasing  $\omega$  (see (3)). The decrease of the lifetime of the quasiparticles limits primarily the possibility of performing experiments on the energy dependence of the renormalization parameter.

Although the influence of the temperature on the renormalization parameter has now been observed for zinc, lead, and probably also mercury (see the reference in [81]), it can obviously be observed also for other metals.

The  $Z(\omega)$  dependence should apparently also be manifest in a change of the specific heat of metals with changing temperature. As a result one should expect deviations from the linear law  $C_e = \gamma T$ , amounting according to the calculations of [83a] to ~20% for Pb and Hg, and apparently about 10% for Sn and In. Obviously, this effect must be taken into account in a rigorous analysis of the specific heat of metals, and primarily when an attempt is made to resolve the specific-heat components due to the electrons and the lattice. Although this effect was first considered in 1962 by Eliashberg [84], it was unfortunately usually disregarded.

## 7. OTHER METHODS OF DETERMINING THE PARAMETERS OF THE ELECTRON-PHONON INTERACTION

In addition to the methods listed above for determining the EPI parameters, other measurements can also be used.

As follows from (1), one can use for this purpose the results of the measurement of the velocity of the normal electrons. In addition to high-frequency methods, one can use for this purpose phenomena connected with the quantization of the energy levels of thin plates of thickness  $d$ , primarily the so-called Tomasch effect, which consists in the following. When the electrons are specularly reflected from the surface of the plate, the energy levels are quantized, with spacings  $\epsilon_q = h\nu/2d$ , in a direction perpendicular to the plane of the plate. Tomasch [85] observed a manifestation of this quantization in the tunnel characteristics of films of superconductors (In, Pb, Sn) with thickness larger than  $2\mu$ .

The quantization was manifested in the form of a system of additional almost equidistant maxima on the characteristics of the tunnel junction. From the distance between the maxima it was possible to measure  $\epsilon_q$  and by the same token the electron velocity. It was shown in the theory of this effect [86] how to reduce the experimental results. The Tomasch effect was used recently to determine the energy dependence of the quasiparticle lifetime [87].

With the aid of the Tomasch effect it is possible to measure simultaneously, with one sample, the gap in the superconducting state and the coefficient of renormalization of the electron velocity in the normal state. Such experiment could yield useful information on the anisotropy of the EPI in metals. Results of a similar experiment for lead were published recently [88].

The tunnel current in the normal state does not depend on the renormalization parameters [89] in the case of a symmetrical barrier. Usually the barrier in the tunnel junction has a certain asymmetry, and from the tunnel characteristics one can obtain certain information on the EPI [90]. Recently, Jouce and Richards [91] observed the manifestation of the EPI in the adsorption of the infrared radiation in lead. All the methods considered above are still in the development stage. So far they have yielded no new characteristics of the EPI. However, since the investigation of the EPI is vigorously pursued everywhere, one can expect in the nearest future new interesting results also in these new directions.

## 8. INFLUENCE OF PRESSURE ON THE ELECTRON-PHONON INTERACTION

Having become acquainted with different methods of EPI investigations and with research devoted to the influence of the electron energy or temperature on the EPI parameters of a given metal, we proceed now to consider a number of studies in which attempts were made to determine the influence exerted on the EPI by different physical characteristics of the substance. All these investigations involve a study of the dependence of the properties of the electron system on external parameters. Such parameters may be the interatomic distance, the degree of physical distortion in the lattice, the number of extraneous impurities, the isotropic composition of the atoms, etc. All these investigations make it possible to compare the effects of the different parameters on the properties of metals.

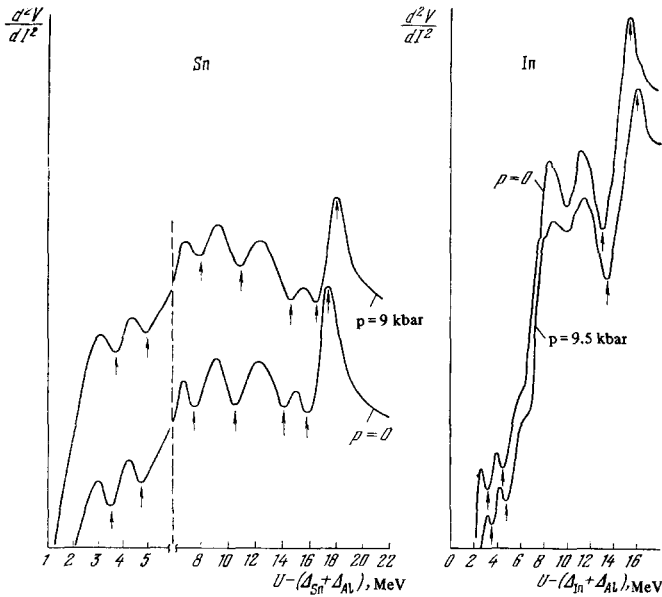


FIG. 6. Pressure-induced displacement of the tunnel characteristics of Sn and In [<sup>67</sup>] (in the case of tin, the scale changes at 6 MeV).

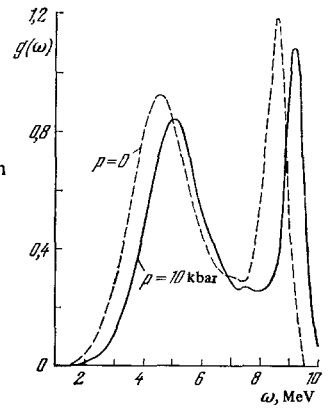
We begin with work on the influence of the hydrostatic pressure on metals. At the present time there are many known studies of the electron structure under pressure. It has been established that the pressure usually leads to a negligible change in the large parts of the Fermi surface (comparable in dimension with the reciprocal lattice); an appreciable change is observed only in some small sections of the surface. Information concerning the change in the characteristics of the phonon spectrum under pressure could be obtained until recently only from indirect measurements, for example from the temperature dependence of the thermal expansion of crystals. Only recently did Frank and Keller<sup>[92]</sup>, Zavaritskiĭ, Itskevich, and Voronovskiĭ<sup>[97,93]</sup>, and Galkin and co-workers<sup>[94]</sup> determine, by the tunnel-effect method, the displacement under pressure of the main singularities of the phonon spectrum of a number of superconductors.

We consider first the results of Zavaritskiĭ et al.<sup>[97]</sup>, who determined the shift of the singularities of the spectrum of the Pb, Sn, or In lattice, the change in the gap, and calculated the change of  $g(\omega)$  of Pb, In, and Sn under pressure. Figure 6 shows the tunnel characteristics of the systems Al-Al<sub>2</sub>O<sub>3</sub>-Sn and Al-Al<sub>2</sub>O<sub>3</sub>-In, plotted at 1°K under a pressure of ~10 kbar and without pressure. The arrows mark the positions of the singularities whose pressure-induced displacements were studied. The numerical characteristics are listed in Table IV.

The results of reconstruction of  $g(\omega)$  for  $P = 0$  and  $P = 10$  kbar show that in the case of lead under pressure we have not only a shift of  $g(\omega)$  along the  $\omega$  axis, in agreement with the data of Table IV, but also an approximate 10% decrease of the absolute value of  $g(\omega)$  without a noticeable change in the Coulomb interaction (Fig. 7). In the case of tin and indium,  $g(\omega)$  is decreased by 4–5% at a pressure of 10 kbar.

The change of  $g(\omega)$  under pressure does not contradict the present-day theoretical concepts. Thus, analyzing the relation (3)–(5), Trofimenkoff and

FIG. 7. Change of the function  $g(\omega)$  of lead under pressure, in accordance with the data of Zavaritskiĭ et al. [<sup>67</sup>].



Carbotte have noted that if the spectrum of the lattice vibration is shifted under pressure by a factor  $\delta$ , then

$$g(\delta\omega) = B\delta^{-2}g(\omega), \quad (22)$$

where  $B \approx 1$  is a coefficient that takes into account the change, under pressure, of the square of the matrix element of the pseudopotential. The change of  $g(\omega)$  at 10 kbar, calculated from (22), amounts to 12–13% for lead, which agrees satisfactorily with the data obtained by reconstructing  $g(\omega)$ .

The results were used to calculate, by means of relation (2) the averaged EPI parameter  $\lambda$  and  $Z$ , which are listed in Table IV, where a summary of the changes in the characteristics of Pb, Sn, In, and Tl under pressure is given. In all the considered metals, the density of the electron states on the Fermi surface  $N$  was measured under pressure<sup>[97,98]</sup>. But corresponding values of  $d \ln N/dp$  are listed in Table IV. We recall, (see relation (1)) that  $N = N_{\text{band}}Z$  and accordingly  $d \ln N/dp = (d \ln N_{\text{band}}/dp) + (d \ln Z/dp)$ . As seen from the table,  $d \ln N/dp \approx d \ln Z/dp$  for all the metals considered. This has made it possible to conclude that the change of the EPI is determined mainly by the dependence of the density of the states of the electrons of Pb, Sn, and In on the lattice parameters.

This conclusion is confirmed also by the following simplest estimates. As is well known<sup>[99]</sup>, the value of  $d \ln N_{\text{band}}/dp$  of Pb, Sn, and In coincides with the value that follows from the free-electron model, or is even smaller. In this model  $d \ln N/dp = -\kappa/3$ , where  $\kappa$  is the compressibility of the matter. Using the data of Table II, we can readily find that  $d \ln Z/dp = \lambda(1 + \lambda)^{-1} \times d \ln \lambda/dp \approx (1/2)d \ln \lambda/dp$  in the case of Pb, Sn, and In; furthermore, using (8) we obtain  $d \ln \lambda/dp \approx (-2)d \ln \langle \omega \rangle /dp$ . For all these metals, as seen from Table IV,  $d \ln \omega/dp \approx 3\kappa$ . Consequently,  $d \ln N_{\text{band}}/dp \approx (1/10)(d \ln Z/dp)$ .

One more manifestation of the singularities of the EPI was noted in a comparison of the pressure-induced changes of the energy gap and of the critical temperature of lead<sup>[93]</sup>. According to the BCS theory, the ratio  $2\Delta_0/kT_C$  is a universal constant for all the superconductors. From the point of view of this theory one should expect the quantities  $d \ln \Delta_0/dp$  and  $d \ln T_C/dp$  to coincide. Actually, however, for most investigated superconductors we have  $|d \ln \Delta_0/dp| > |d \ln T_C/dp|$  (see Table IV). This difference is largest for lead. It was known earlier<sup>[100]</sup> that the de-

duction of the BCS theory, that  $2\Delta_0/kT_C$  is constant, is not quite accurate. Actually this ratio increases somewhat with  $T_C/\Theta_D$ .

Geilikman and Kresin<sup>[101]</sup>, analyzing this question within the framework of the equations derived by Eliashberg, have shown that actually

$$2\Delta_0/kT_C = 3.52 [1 + 5.3 (T_C/\omega_0)^2 \ln(\omega_0/T_C)], \quad (23)$$

where  $\omega_0$  is the characteristic energy of the phonons interacting with the electrons. Using (23), Geilikman and Kresin were able to explain the increase of  $2\Delta_0/kT_C$  of lead and mercury, although they have assumed that the electrons interact only with the longitudinal phonons.

The results of the reconstruction of  $g(\omega)$  show that actually transverse phonons participate in the interaction. Moreover, all the relations contain  $g(\omega)/\omega$ , and even if  $g(\omega)$  differs from zero in a wide energy interval, the main contribution to all the effects is made by the region of low energies. Thus, these are phonons with energy  $\sim 4.5$  MeV the case of lead and  $\sim 6$  MeV in the case of tin and indium, although the lattice-vibration spectra of the last two metals extend to  $\sim 18$  MeV. If this is taken into account and  $\omega_0$  in (22) is replaced by the energy corresponding to the maximum of  $g(\omega)/\omega$ , then we obtain for lead values of  $2\Delta_0/kT_C$  that practically coincide with the experimental value (see<sup>[93]</sup>).

The ratio  $\omega/T_C$  of semiconductors usually increases under pressure. As a result, the ratio  $2\Delta_0/kT_C$  approaches the value 3.52. If we calculate  $d \ln \Delta_0/dp$  for Pb, Sn, and In from relation (23), and the values of  $d \ln T_C/dp$  and  $d \ln \omega/dp$ , then the obtained values turn out to be in good agreement with the experimental results (see Table IV).

The quantity  $d \ln \Delta_0/dp$  was included in the pro-

gram for reconstructing  $g(\omega)$  and naturally cannot be used to verify the theory. The quantity  $d \ln T_C/dp$ , calculated from  $\lambda$ ,  $d\lambda/dp$ , and  $d\omega/dp$  with the aid of the McMillan relation (12) is shown in Table IV. As seen from the table, the McMillan equations can be used only in first approximation to calculate the changes of  $T_C$  under pressure.

The main experimental results of Franck and Keller<sup>[92]</sup> and Galkin et al.<sup>[94]</sup>, are listed in the table. The results of Franck and Keller are less reliable than the remaining ones, since the authors were able to perform the measurements only up to 3.3 kbar at 2°K. In the remaining studies, the measurements were made up to 15 kbar. The reconstruction of  $g(\omega)$  of lead was also carried out by Franck et al.<sup>[102]</sup>. According to the figure of that article, no decrease of  $g(\omega)$  under pressure was observed. According to the estimates in<sup>[67]</sup> it should amount to  $\sim 3\%$  at 3.3 kbar, which is close to the possible error in the program for reconstructing  $g(\omega)$ . The values of  $g(\omega)$  and  $d\lambda/dp$  given in that reference, however, coincide with the results of Zavaritskiĭ, Itskevich, and Voronovskii<sup>[67]</sup>. Analysis of the change of  $T_C$  of superconductors under pressure, on the basis of the equations of McMillan, was made also in the review of Boughton et al.<sup>[103]</sup> and in<sup>[18]</sup>.

At the present time, we see no noticeable discrepancy in the different measurements of the characteristics of superconductors under pressure. In all the investigated metals, the change of the EPI is determined mainly by the displacement, under pressure, of the spectrum of the lattice vibrations. This effect plays the predominant role in comparison with the pressure-induced change of the electron Fermi surface. This conclusion cannot be extended, of course, to all metals. It pertains probably only to most non-transition metals. We shall return to this question later on.

Table IV

Measured quantity x	Lead			Tin			Indium			Thallium		
	x	$\frac{dx}{dp} \cdot 10^6, \text{bar}^{-1}$	$\frac{d \ln x}{dp} \cdot 10^6, \text{bar}^{-1}$	x	$\frac{dx}{dp} \cdot 10^6, \text{bar}^{-1}$	$\frac{d \ln x}{dp} \cdot 10^6, \text{bar}^{-1}$	x	$\frac{dx}{dp} \cdot 10^6, \text{bar}^{-1}$	$\frac{d \ln x}{dp} \cdot 10^6, \text{bar}^{-1}$	x	$\frac{dx}{dp} \cdot 10^6, \text{bar}^{-1}$	$\frac{d \ln x}{dp} \cdot 10^6, \text{bar}^{-1}$
$T_C, ^\circ\text{K}$	7.2		-5.3 [-11.8] *	3.79		-13.3 [-14.5] *	3.4		-12.6 [-17] *	2.4		
$2\Delta_0, \text{MeV}$	2.7	-21.6 ± 2*** 27 ± 2.5 b 22.2 ± 1 c	-8.0 -10.0 -8.0 [-9.5] ***	1.2	-18 ± 1 a -18.5 ± 1 c	-15 [-14.8] ***	1.02	-14.5 ± 0.6 a -14.3 ± 1.3 c	-14.2 [13.7] ***			2.8 ± 1.3 c
$\omega_e, \text{MeV}$	3.8	32 ± 7 a 26 ± 4 c	8.4	3.5	22 ± 4 a	6.3	8.25	21 ± 3 a	6.5	3.99	14.8 ± 7 c	3.7
	4.45	36 ± 5 a 33 ± 4 c	8.0	4.8	22 ± 10 a	4.6	4.6	26 ± 4 a	5.7	9.5	5.45 ± 1 c	5.8
	4.9	32 ± 7 a 33 ± 4 c	6.5	7.6	50 ± 20 a	6.5	12.9	48 ± 5 a	3.7			
	4.45 ( $\omega_T$ )****)	40 ± 4 a 24 ± 3 b	9.0	10.6	42 ± 5 a	4.0	15.0 ( $\omega_e$ )	75 ± 10 a	5.0			
	8.45 ( $\omega_L$ )	60 ± 6 a 59 ± 6 b	7.1	14.2	55 ± 7 a	3.9						
	9.9 ( $\omega_e$ )	64 ± 4 c 70 ± 10 a	7.1	15.9	67 ± 7 a	4.2						
				17.4 ( $\omega_n$ )	70 ± 14 a	4.0						
$\lambda$	1.49	-28 ± 2 a	-18.8	0.79	-6.3 ± 0.7 a	-8	0.82	-8.0 ± 0.8 a	-9.8			
$Z$	2.49	-28 ± 2 a	-11 ± 1	1.79	-6.3 ± 0.7	-3.4 ± 0.4	1.32	-8.0 ± 0.8 a	-4.4 ± 0.4			
$N/x$		2.28	-8.3 ± 1.5 97		1.81	-3.6 ± 0.5 98		2.39	-3.6 ± 0.7 98			2.73

\*The numbers in the square brackets are obtained by calculation from McMillan's relation (12).  
 \*\*The superscripts a, b, and c denote the data of Zavaritskiĭ et al. [67,93], the data of Franck and Keller [92], and the data of Galkin et al. [94,96], respectively.  
 \*\*\*Calculation in accordance with the Geilikman and Kresin relation (23), with  $d \ln T_C/dp$  and  $d \ln \omega/dp$  from the table.  
 \*\*\*\*The center of gravity of the envelope curve  $d^2V/dl^2$  at  $T > T_C$  of Al.

### 9. ELECTRON-PHONON INTERACTION IN METALS WITH EXTREMELY DISTORTED LATTICE

Experiments with pressure show that within the framework of the EPI theory it is possible to explain the dependence of the electronic properties of lead, tin, and indium on the interatomic distance. It is natural to attempt to consider within the framework of these concepts also the properties of metals having an extremely distorted crystal lattice. Such distortions can be produced by condensation of the metal at helium temperatures.

Back in 1938, Shal'nikov<sup>[104]</sup> observed that the critical temperature of tin increases if the sample is prepared by condensation on a surface cooled to helium temperatures. Subsequent experiments<sup>[105, 106]</sup> have shown that these effects take place not only for tin, but for most other superconductors, while Buckel and Hilsch<sup>[106]</sup> have established that the relative increase of  $T_c$  depends on the ratio  $T_c/\Theta_D$ .

To obtain additional information on the properties of metals obtained under such anomalous conditions, the present author undertook to investigate the EPI by the tunnel-effect method for a number of superconductors condensed at helium temperatures. The investigations initiated in<sup>[107, 108]</sup> were subsequently continued in other countries<sup>[109-112]</sup>. Tests were made on Al<sup>[107]</sup>, In<sup>[108]</sup>, Sn<sup>[108, 110]</sup>, Pb<sup>[107, 108, 110]</sup>, Bi<sup>[108-111]</sup>, Ga<sup>[108, 109, 112]</sup>. In<sup>[108]</sup>, the tunnel junctions were prepared in the glass tube shown in Fig. 8. The films were evaporated on the bottom of a small glass vessel 1. Electric contact with the films was produced through platinum contacts 2 deposited by cathode sputtering and by platinum leads 3 fused into the glass. The shape of the film was determined by moving screens 4 secured to the small vessel by wire 5. The metal was evaporated from

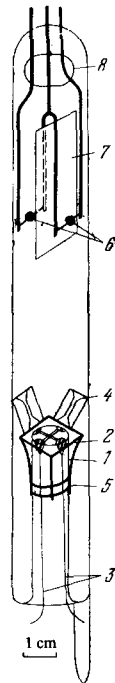


FIG. 8. Instrument used by the author<sup>[108]</sup> for the investigation of superconductors prepared by condensation at low temperatures.

previously heat-treated coils 6; the screen 7 protected the evaporator from mutual contamination. The glass insulator 8 secured the evaporators.

The sample was prepared in the following sequence. The assembled instrument was heated at  $\sim 500^\circ\text{K}$  in a vacuum up to  $10^{-6}$  Torr. An aluminum layer was then evaporated at  $300^\circ\text{K}$ . Highly dehydrated air was admitted into the instrument to a pressure 400 Torr, and the aluminum was oxidized at  $500^\circ\text{K}$  to produce an  $\text{Al}_2\text{O}_3$  film. The oxidation time ranged from 2 to 12 hours, depending on the investigated metal. After the oxidation, the instrument was evacuated and sealed. During the time of evaporation of the investigated metal, the instrument was immersed completely in liquid helium maintained at temperature below  $2^\circ\text{K}$ .

By varying the pressure over the liquid helium in the helium bath it was possible to perform measurements in the interval  $1-4.2^\circ\text{K}$ . To obtain higher temperatures, a miniature heater and a carbon resistance thermometer were placed inside the cavity of the small vessel 1 of the instrument. By measuring the power released in the heater it was possible to carry out measurements in the range  $4.2-30^\circ\text{K}$  in an instrument completely immersed in liquid helium.

In the experiment we usually recorded the characteristics  $dV/dI$  and  $d^2V/dI^2$  as functions of the voltage  $V$ , and the gap  $\Delta_0$  was primarily determined from these characteristics. The values of  $\Delta_0$  and  $T_c$  for all the investigated metals are indicated in Table V, which gives the different characteristics of the superconducting metals condensed at helium temperatures.

The characteristics of all the investigated systems reveal at  $eV > \Delta_0$  singularities that could be clearly registered on the  $d^2V/dI^2$  characteristics. These singularities appear on the  $d^2V/dI^2$  curves in the form of a series of maxima and minima, the positions of which are practically independent of the temperature. The amplitudes of these singularities decrease gradually when the temperature is raised to  $T_c$ , where they vanish. After heating the samples to room temperature, these singularities go over smoothly into singularities that are usually attributed to  $g(\omega)$ . It was natural to assume that the singularities of the tunnel characteristics of a metal condensed at helium temperatures are connected by relation (10) with the function  $g(\omega)$  at  $eV > \Delta_0$ .

To reconstruct  $g(\omega)$  it is necessary first to determine  $R(V) = (dI_S/dV)(dI_N/dV)^{-1}$ . In the case of films condensed at low temperature, additional difficulties arise here. The point is that the quantity  $dI_N/dV$  can depend on the voltage. Usually to measure this quantity accurately the superconductivity of the metal is destroyed by an external magnetic field. For a metal condensed at  $1^\circ\text{K}$ , the critical magnetic field is very large (for example,  $H_c \approx 10^5$  Oe for Bi at  $1^\circ\text{K}$ <sup>[114]</sup>), and this method of determining  $dI_N/dV$  is difficult. The values of  $(dI_N/dV)(V_{T=1^\circ\text{K}}$  in experiments with metals condensed at  $2^\circ\text{K}$  were therefore determined usually by extrapolating the measurements performed at  $T > T_c$ . This, naturally, gave rise to a large error in the value of  $dI_N/dV$  and by the same token in the value of  $R(V)$ . According to the data of<sup>[108]</sup>, the relative error in the value of  $R(V)$  can reach  $3 \times 10^{-3}$ , which is comparable with the magnitude of the effect

used in the calculations of  $g(\omega)$ . Thus, the deviation of  $R(V)$  from the predictions of the BCS theory amounts in the case of lead, bismuth, gallium, and tin to  $30 \times 10^{-3}$ ,  $20 \times 10^{-3}$ ,  $10 \times 10^{-3}$ , and  $7 \times 10^{-3}$ , respectively.

Figure 9 shows most of the known attempts to reconstruct  $g(\omega)$  for different metals condensed at helium temperatures. Some numerical characteristics are given in Table V. Although the results indicate in general a similar character of the variation of  $g(\omega)$ , the curves differ noticeably in their details. This difference can be due to two factors. First,  $g(\omega)$  were calculated in accordance with different programs, and the relative error in  $g(\omega)$  reconstructed from the data of  $R(V)$  curve could reach, according to<sup>[108]</sup>, 10–15%. Second, discrepancies in the  $R(V)$  curves used for the calculation are possible for all metals. In those cases when numerical data are given for the calculation, this difference is usually noticeable. The discrepancy is particularly large in the case of Bi, amounting to  $5 \times 10^{-3}$  between the data of<sup>[108]</sup> and<sup>[109]</sup>. Taking all the foregoing into account, it is not surprising that there is no complete agreement between the calculated function  $g(\omega)$ .

Let us examine the change of  $g(\omega)$  as a result of low-temperature condensation. Comparing Figs. 2–4 and 9 we see that the change of  $g(\omega)$  occurs in two directions; first, the singularities of the  $g(\omega)$  curve becomes smeared out, and accordingly all that remains pronounced on the  $d^2V/dI^2$  curve is the maximum corresponding to the longitudinal modes and to the end point of the lattice vibration spectrum. Second, there is an appreciable increase of  $g(\omega)$  at low energies, and a smearing of the corresponding maximum up to  $\omega = 0$ .

The shift of the center of gravity of the entire  $g(\omega)$  curve in the region of small energies, and the decrease of  $\langle \omega \rangle$ , cause an increase of the EPI. As a result, all the superconducting properties of the metal are changed.

As is well known, the width of the gap  $\Delta_0$  is used to reconstruct  $g(\omega)$ . By the same token, obviously, within

the framework of the theory describing the EPI, the increase of  $\gamma_0$  and accordingly of  $T_C$  can be attributed in natural fashion to the change of  $g(\omega)$ . The shift of the maximum of  $g(\omega)$  into the region of low energies should lead also to an increase of the ratio  $2\Delta_0/kT_C$ . In Table V are shown, for all the metals condensed at low temperatures, the values of  $2\Delta_0/kT_C$ , calculated from the relation (23), and the values of  $T_C$  calculated from (13). As seen from the table, they are in satisfactory agreement with the experimental data.

Experiments with pressure show that the change of  $g(\omega)$  is determined primarily by the change in the spectrum of the lattice vibrations. Obviously, this takes place also in the case of a metal condensed at low temperatures. Although all these ideas have been under development since our 1967 papers, one cannot indicate unambiguously at the present which mechanism causes the change of the lattice-vibration spectrum. This may be connected, for example, with the appearance of additional lattice-vibration modes near the lattice defect, with an increase in the amplitude of the vibrations in the lattice, with dislocations, etc. The last model was considered in detail by Garland et al.<sup>[48D]</sup>. In particular, they were able to explain the result of Buckel and Hilsch concerning the connection between the relative increase of  $T_C$  and the ratio  $T_C/\Theta_D$ . This conclusion follows from relation (12), which shows that  $dT_C/d\lambda$  should decrease sharply with increasing  $\lambda$ .

At the present time the idea that the increase of the critical temperature of superconductors condensed at low temperature is connected with a change in the spectrum of the lattice vibrations is apparently universally accepted. These representations were used later also to explain the increase of the critical temperature of finely granulated samples<sup>[115]</sup>, a number of alloys with unstable lattices, etc.

A number of recent publications are devoted to the properties of superconductors that are condensed at low temperatures<sup>[116]</sup> and likewise confirm the ideas presented above.

Table V

Metal	Reference	$T_C$ , °K	$2\Delta_0$ , MeV	$\frac{2\Delta_0}{\hbar T_C}$	$\omega_1$	$\omega_2$	$\omega_e$	$\langle \omega \rangle$	$\lambda$	$u^*$	$[T_C]$ , °K
Ga	108	8.4	3.12	4.25 (4,3)*	5	18	25	5.8	1.4	0.1	7.2
	109	8.56	3.32	4.5	3	17.5		5.47	2.25	0.17	8.5
	111	8.47	3.29	4.5							
	112	8.4	3.30	4.5							
	113	8.45	3.02	4.1							
Pb	108	7.2	2.82	4.5 (4,5)*	4.5	8.5	10	3.8	2.8	0.1	7.6
	110	7.2	2.70	4.4				3.74	1.91	0.008	6.3
Bi	108	6	2.37	4.6 (4,5—4,3)*	3–3.5	8.5	12	2.9	2.7	0.1	5.8
	109	6.11	2.42	4.59	2.2	8.5		2.86	2.45	0.1	5.4
	111	5.93	2.33	4.56							
	110	6.1	2.44	4.6				2.98	1.85	0.01	5.7
	113	6.11	2.2	4.2							
Sn	108	4.2	1.5	4.05 (4)*	3.5–4	14	17.5	4.9	1.6	0.1	6.6
	110	4.5	1.54					7.9	0.84	0.07	5.6
In	4	2–	1.7–			13.5	16				
	108	3.8	—1.3**)								

\* $2\Delta_0/kT_C$  was calculated from  $\omega_1$ ,  $T_C$ , and relation (23) of Geilikman and Kresin<sup>[101]</sup>;  $\omega_1$  and  $\omega_2$  are the positions of the maxima of  $g(\omega)$ ,  $\omega_e$  is the end point of the spectrum,  $\langle \omega \rangle$  was calculated according to (14) (all in MeV);  $[T_C]$  was calculated using  $\lambda$ ,  $\langle \omega \rangle$ , and McMillan's relation (13).

\*\*Depends on the thickness of the In film.

## 10. ELECTRON-PHONON INTERACTION IN ALLOYS OF NONTRANSITION METALS

We shall consider investigations of EPI in alloys by the tunnel-effect method. The following systems were investigated Pb - In<sup>[117,118]</sup>, Pb - Tl<sup>[118a,119]</sup>, Pb<sub>1-2x</sub>Bi<sub>x</sub>Tl<sub>x</sub><sup>[120]</sup>, In - Tl<sup>[61]</sup>. Samples with a given chemical composition were usually prepared by successive complete evaporation of many (~100) small pieces of an alloy with given concentration.

We consider first the results obtained with the PbIn system. As is well known<sup>[121]</sup>, Pb and In form a system of substitution solid solutions in a wide range of concentrations. The atomic weights of Pb and In differ by a factor of almost two, and this system is convenient for the study of the changes of the EPI or the spectrum of the lattice vibrations when atoms with strongly different masses penetrate into the lattice. Figure 9 shows the reconstructed  $g(\omega)$  for this system in accordance with the data of<sup>[117]</sup> and<sup>[118b]</sup>.

The penetration of an impurity changes  $g(\omega)$  of lead in two ways. First, the principal maxima of the lead are broadened somewhat and their amplitudes are decreased. Second, a new additional maximum of the function  $g(\omega)$  appears at 9.5 MeV. This maximum is probably connected with the local impurity-atom modes considered by I. M. Lifshitz<sup>[122,123]</sup>. The theory of<sup>[123]</sup> makes it possible to calculate the position of the additional maximum, which turned out to agree with the experimental data<sup>[117]</sup> (see also<sup>[131]</sup>).

As seen from Fig. 10, the additional maximum does not change its position when the indium content is increased up to 25%. With further increase of the impurity content, it shifts towards higher energies. The probable cause is that whereas at relatively low concentrations the indium atoms are in the field of the lead atoms, when the impurity content is increased interactions between neighboring indium atoms come into play. As a result, the maximum shifts towards the position of the corresponding maximum of  $g(\omega)$  of indium, which is located at 13 MeV. We note that in this case one deals with a maximum due to the extremely short-wave lattice vibrations.

Local impurity-atom modes were observed so far only in the Pb-In systems. Attempts to observe the modes in other systems were unsuccessful. This pertains, according to the data by the author, to atoms introduced by the method of low-temperature simultaneous condensation.

The system In-Tl has a different behavior. When the Tl concentration is increased<sup>[121]</sup> the system goes over in succession from a face-centered tetragonal lattice to a face-centered cubic lattice (at ~20% Tl) and then (at 50–70% Tl) to a body-centered cubic lattice, and finally to the hexagonal lattice of pure thallium<sup>[121]</sup>.

The reconstructed functions  $g(\omega)$  for each of the modifications are shown in Fig. 11. Each of the curves shows the results of an x-ray diffraction investigation of the structure of the corresponding sample. The experimental data show that for the face-centered tetragonal and face-centered cubic modifications the function  $g(\omega)$  are very similar. The  $g(\omega)$  curves show two easily distinguishable peaks, which pertain to the transverse and longitudinal vibration modes. The  $g(\omega)$  of a body-centered cubic system has three distinct peaks, two corresponding to two transverse modes and one corresponding to a longitudinal mode. The hexagonal system is characterized by the presence of a sharp peak at low energies and a number of weaker maxima at higher energies. It is seen from Fig. 10 that the function  $g(\omega)$  of the sample with body-centered cubic lattice is noticeably shifted towards lower energies in comparison with  $g(\omega)$  of other samples. If the shift into the region of low energies, due to the presence of the low-lying modes, is typical of a body-centered cubic structure, then it becomes understandable why superconductors with body-centered cubic lattices have the highest critical temperature. This tendency is clearly noticeable for the In-Tl system. The maximum  $T_C$  is possessed by the sample with the body-centered cubic structure.

Dynes also points out that the transition from the face-centered to the body-centered cubic structure is not accompanied by a qualitative change of  $g(\omega)$  and

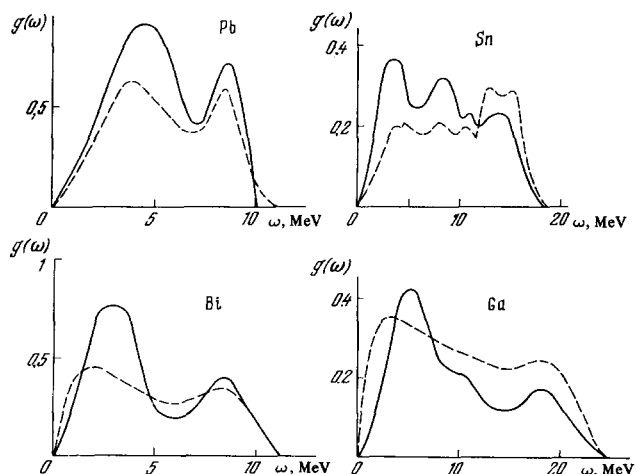


FIG. 9. The functions  $g(\omega)$  for Pb, Sn, Bi, and Ga, obtained by condensation at low temperatures. Solid curves—the author's data<sup>[108]</sup>, dashed curve for Sn and Pb—data of<sup>[10]</sup>, for Bi and Ga—data of<sup>[109]</sup>.

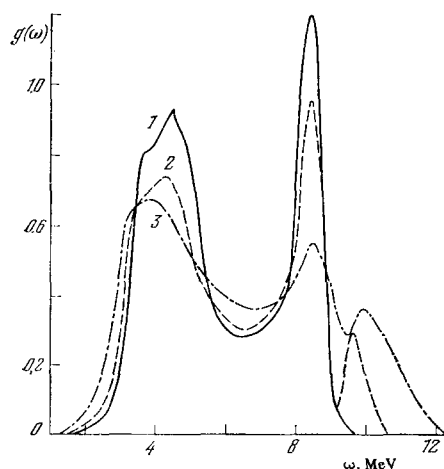


FIG. 10. The function  $g(\omega)$  for the alloys Pb-In<sup>[117,118b]</sup>. 1—Pure lead, 2—Pb<sub>0.75</sub>In<sub>0.25</sub>, 3—Pb<sub>0.6</sub>In<sub>0.4</sub> (curves from<sup>[118b]</sup>).

is possibly close to a second-order phase transition.

The maxima of  $g(\omega)$ , especially the one corresponding to the longitudinal modes, are noticeably smeared out. This is evidence that the phonons have a finite lifetime in a nonideal lattice. The relative smearing of the  $\Delta\omega/\omega$  maximum near pure In or Tl is proportional to the impurity concentration.

The smearing of the maxima of  $g(\omega)$  were observed also in other investigations of alloys. This phenomenon is typical of a nonideal structure. As shown by Knorr and Barth<sup>[110]</sup>, even for films condensed at low temperature it is still possible to increase the widths of the maxima of  $g(\omega)$  by simultaneous condensation of a metal and a dielectric.

For a number of alloys investigated by the tunnel effect method there are known also neutron-diffraction measurements of the lattice-vibration spectrum<sup>[124]</sup>. The phonon density of states  $F(\omega)$  calculated from the neutron-diffraction data agrees satisfactorily<sup>[118b, 125]</sup> with  $g(\omega)$ .

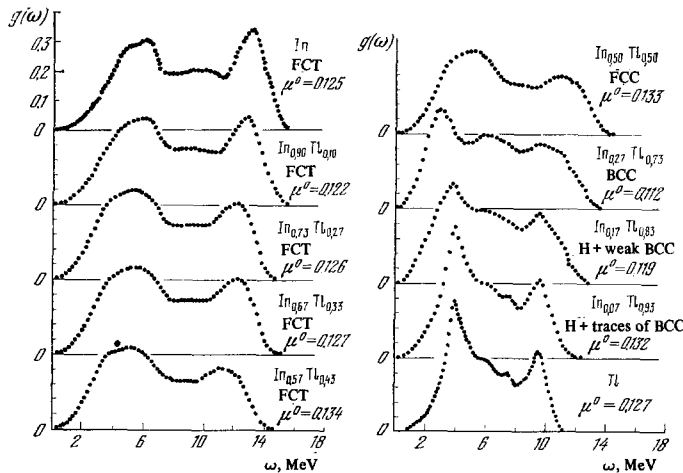


FIG. 11. The function  $g(\omega)$  for the system In-Tl in accordance with the data of [61]. The results of x-ray diffraction investigations of the alloy and the values of  $u^* = \mu_0$  used in the calculation of  $g(\omega)$  are marked on each curve.

11. ELECTRON-PHONON INTERACTION IN TRANSITION METALS

The internal shells of the atoms of transition metals are not filled, and it is impossible to separate in the unit cell an ionic core with localized internal shells of the atom. As a result, one of the main premises of the pseudopotential theory is violated here; relations (2)–(6) can therefore not be used to calculate the EPI. However, it is still possible to use here all the relations based on the Eliashberg equations (10), from which it is also possible to calculate the value of the parameter  $\lambda T_C$ .

The electronic bands connected with the internal shells of the atoms are usually narrower than the bands due to the external shells. The density of the electronic states is accordingly larger. Consequently, the specific heat of the electrons of most transition metals greatly exceeds the specific heat of nontransition metals. In addition, in this case the density of the electron states depends nonmonotonically on the electron energy or on the number of the electrons per atom. This makes it possible for small impurities to alter significantly the density of states of the electrons. On the basis of this circumstance we can attempt to use the results of the investigation of the characteristics of transition-metal alloys to assess the role of the density of states of electrons in the EPI parameters.

Table VI shows the results of the investigation of most binary alloys of transition metals of superconductors. Table VI was compiled by using the data of [13, 127]. The values of  $\lambda$  given in the table were calculated from  $T_C$  and  $\Theta_D$  with the aid of the inverted relation (12). The density of electrons per atom  $N_{band}$  was calculated from the relation

$$N_{band} = 3\gamma/2\pi^2k^2(1 + \lambda).$$

Comparing the characteristics of different superconductors, McMillan<sup>[13]</sup> pointed out that in body-centered metals  $N_{band}\langle q^2 \rangle$  in relation (8) for  $\lambda$  changes by not more than 1.5–2 times when  $N_{band}$  is changed by up to 10 times.  $N_{band}\langle q^2 \rangle \sim 7 \text{ eV}/(\text{\AA})^2$ .

Table VI

Metal and alloy	$T_C$ , °K	$\Theta_D$ , °K	$\gamma$ , mJ/g-mole (°K) <sup>2</sup>	$N_{band}$ , st/eV-atom	$\lambda$	$10^3 \lambda / N_{band}$ (M)	Metal and alloy	$T_C$ , °K	$\Theta_D$ , °K	$\gamma$ , mJ/g-mole (°K) <sup>2</sup>	$N_{band}$ , st/eV-atom	$\lambda$	$10^3 \lambda / N_{band}$ (M)
Ti	0.39	426	3.32	0.52	0.38	1.55	Mo	0.92	460	1.87	0.42	0.41	1.02
Ti <sub>0.8</sub> V <sub>0.2</sub>	3.5	235	6.9	1.46	0.54	0.77	Ta	8.22	351	4.4	0.57	0.5	0.89
Ti <sub>0.7</sub> V <sub>0.3</sub>	6.44	244	10.0	4.31	0.62	0.99	Ru	0.49	550	3.0	0.46	0.38	0.84
Ti <sub>0.5</sub> V <sub>0.5</sub>	7.3	262	10.8	4.39	0.65	0.95	La	4.9	142	9.4	1.12	0.85	0.55
Ti <sub>0.25</sub> V <sub>0.75</sub>	7.16	279	10.6	1.36	0.65	0.95	Hf	0.09	252	2.16	0.34	0.34	0.56
Ti <sub>0.15</sub> V <sub>0.85</sub>	7.02	283	10.3	1.32	0.65	0.98	Ta	4.48	258	6.0	0.77	0.65	0.47
V	5.3	399	9.9	1.31	0.60	0.90	W	0.012	390	0.9	0.15	0.28	0.82
V <sub>0.9</sub> Cr <sub>0.1</sub>	3.21	370	8.15	1.13	0.53	0.92	W <sub>0.5</sub> Re <sub>0.1</sub>	0.7	375	1.63	0.24	0.42	0.96
V <sub>0.8</sub> Cr <sub>0.2</sub>	1.90	400	7.15	1.02	0.48	0.92	W <sub>0.85</sub> Re <sub>0.15</sub>	2.26	365	2.4	0.29	0.5	0.94
V <sub>0.75</sub> Cr <sub>0.25</sub>	1.36	425	6.75	0.99	0.45	0.96	W <sub>0.8</sub> Re <sub>0.2</sub>	3.2	359	2.2	0.3	0.54	0.98
V <sub>0.6</sub> Cr <sub>0.4</sub>	0.37	450	5.40	0.83	0.38	0.96	W <sub>0.75</sub> Re <sub>0.25</sub>	4.64	351	2.30	0.3	0.6	1.10
V <sub>0.5</sub> Cr <sub>0.5</sub>	0.1	470	4.85	0.77	0.33	0.84	W <sub>0.12</sub> Re <sub>0.88</sub>	4.47	332	3.76	0.47	0.7	0.82
Zr	0.55	290	2.79	0.42	0.41	1.07	Re	1.65	415	2.3	0.33	0.46	0.75
Zr <sub>0.5</sub> Nb <sub>0.5</sub>	9.3	238	8.3	0.93	0.88	1.03	Os	0.65	500	2.3	0.35	0.339	0.59
Zr <sub>0.25</sub> Nb <sub>0.75</sub>	10.8	246	8.9	0.98	0.93	1.02	Ir	0.14	420	2.2	0.51	0.32	0.35
Nb	9.2	277	7.8	0.91	0.82	0.97	Mo <sub>0.95</sub> Re <sub>0.05</sub>	1.5	450	2.2	0.32	0.45	1.41
Nb <sub>0.85</sub> Mo <sub>0.15</sub>	5.85	265	6.3	0.79	0.70	0.96	Mo <sub>0.9</sub> Re <sub>0.1</sub>	2.9	440	2.6	0.36	0.51	1.36
Nb <sub>0.6</sub> Mo <sub>0.4</sub>	0.6	371	2.87	0.43	0.41	1.03	Mo <sub>0.8</sub> Re <sub>0.2</sub>	8.5	420	3.8	0.48	0.68	1.25
Nb <sub>0.4</sub> Mo <sub>0.6</sub>	0.05	429	1.62	0.26	0.31	1.27	Mo <sub>0.7</sub> Re <sub>0.3</sub>	1.08	395	4.1	0.49	0.70	1.26
Nb <sub>0.3</sub> Mo <sub>0.7</sub>	0.016	442	1.42	0.24	0.29	1.25	Mo <sub>0.6</sub> Re <sub>0.4</sub>	1.26	340	4.4	0.5	0.86	1.27
Nb <sub>0.2</sub> Mo <sub>0.8</sub>	0.095	461	1.49	0.24	0.33	1.45	Mo <sub>0.5</sub> Re <sub>0.5</sub>	1.15	320	4.4	0.5	0.85	1.20
Nb <sub>0.1</sub> Mo <sub>0.9</sub>	0.3	483	1.67	0.26	0.36	1.46							

This has enabled him to advance the hypothesis that the EPI parameters of transition metals are determined only by the characteristics of the lattice-vibration spectrum,  $M\langle\omega^2\rangle$  and

$$\lambda = c/M\langle\omega^2\rangle. \quad (24)$$

If, however, we turn to the data of Table VI, then we can note that for one class of substances,  $N_{\text{band}} \otimes D$  also remains constant with the same accuracy, and consequently  $\lambda \approx N_{\text{band}}$ . The existence of a dependence of  $\lambda$  on  $N_{\text{band}}$  or  $\gamma$  was noted earlier both in McMillan's paper<sup>[13]</sup> and in the communication of Ishikawa and Toth<sup>[126]</sup>. Moreover, it turns out (see Table VI) that for almost all the binary alloys of the transition metals  $\lambda/N_{\text{band}}\langle M \rangle \approx \text{const} = 10^{-2}$ , and accordingly

$$\lambda = 10^{-2}N_{\text{band}}\langle M \rangle, \quad (25)$$

where  $\langle M \rangle$  is the average mass of the atoms of the alloy.

Although relation (25) does make it possible to determine the value of the EPI from the parameters of the alloy with good accuracy, one can hardly ascribe too much significance to this empirical relation, and incidentally also to relation (24); all the more, one can not conclude on this basis that any of the factors in the EPI of transition metals predominates. In this case an important role is apparently played both by the change of  $N_{\text{band}}$  and by the change of the lattice vibration spectrum.

For example, it is known (see the review<sup>[103]</sup>) that  $dT_C/dp \gtrsim 0$  for a number of transition metals. If it is recognized that the frequencies of the lattice vibration spectrum increase under pressure, then it is difficult to explain this effect within the framework of the dependence of  $\lambda$  only on  $\langle\omega^2\rangle$ . To explain these results it is probably necessary to consider also the change of  $N_{\text{band}}$ .

An increase of the critical temperature of a superconductor under pressure was observed also for a number of nontransition metals and alloys<sup>[128-130]</sup>. In this case, however, the increase of  $T_C$  occurs only in a limited range of pressures, after which, as for most superconductors,  $T_C$  begins to decrease with further increase of pressure. This anomalous change of  $T_C$  under pressure was explained by Makarov and Bar'yakhtar<sup>[129]</sup> by assuming a partial restructuring of the Fermi surface under pressure. Alekseevskii<sup>[130]</sup>, however, relates a similar change of  $T_C$  under pressure with the anomalous restructuring of the lattice-vibration spectrum.

As is well known, the electron and phonon systems can be considered to be independent in metals only in first approximation. Actually, each change of the electron system leads to a change in the phonon system. Consequently, additional difficulties arise when it comes to determine the dependence of the EPI on the electron density. There is no doubt that additional research is necessary here.

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