INCREASE OF THE CRITICAL TEMPERATURE OF SUPERCONDUCTORS CONDENSED AT LOW TEMPERATURES

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Results are presented of the investigation of the tunnel effect in Bi, Ga, Pb, Sn, In and Al condensed at 2°K. In all the metals studied, an increase has been observed in the gap width Δ_0 and ratio $2\Delta_0/kT_c$ due to low-temperature condensation. Singularities related to the lattice oscillation spectrum (which was established for a number of metals) have been observed in the tunnel characteristics of all investigated metals for $eV > \Delta_0$. The results are employed to explain the increase in the critical temperature of superconductors condensed at low temperatures.

In 1939, Shal'nikov[1] discovered that the critical temperature and critical magnetic field of Sn increase if the sample is prepared by condensation of the metal on a surface cooled to helium temperatures. Experiments carried out subsequently[2-4] have shown that these effects take place not only in Sn but also in a majority of other superconductors. However, although the increase of the critical magnetic field was explained as early as 1952 within the framework of representations of type II superconductors,[3] there has been no way to date to explain the increase in the critical temperature of the superconductors. It has been reliably established only that the relative increase in the critical temperature evidently depends on the ratio T_c/Θ (Θ is the Debye temperature)[2] and the amount of distortion of the crystal lattice.[4] The present research was undertaken with the aim of obtaining additional information on the properties of superconductors, condensed at low temperatures, with the hope that this information would lead to the discovery of ways to explain the increase of their critical temperature.

The tunnel effect was chosen as the method for investigation, since it makes it possible to obtain detailed information on the investigated effect. As is known (for example,[5]) the current I_{sn} through the normal metal-superconductor junction at a temperature T = 0 is equal to

$$I_{sn} = C\int_0^V N_s(\omega)\,d\omega, \quad N_s(\omega) = N_n\,\mathrm{Re}\frac{|\omega|}{(\omega^2-\Delta^2)^{1/2}}, \qquad (1)$$

where Δ is the gap width in the spectrum of electrons of the superconductor; N_s, N_n are the densities of states of electrons in the normal and superconducting states, respectively. Hence

$$\frac{dI_{sn}}{dV}\Big/\frac{dI_{nn}}{dV} = \frac{N_s}{N_n} = \mathrm{Re}\frac{|\omega|}{(\omega^2-\Delta^2)^{1/2}} \approx 1 + \frac{\mathrm{Re}\,\Delta^2(\omega)}{2\omega^2} = 1 + n(\omega). \qquad (2)$$

It is evident that the characteristics of the transitions I(V) or dV/dI = f(V) allow one to determine the gap width Δ and the function Re $\Delta^2(\omega)$ for $eV > \Delta$. The quantity $\Delta(\omega)$ is determined in the case of electron-phonon interaction by the following set of equations, as was shown by Eliashberg.[6] The equations are written in integral form:[5]

$$\Delta(\omega) = \varphi(\omega)/Z(\omega), \qquad \Delta(\Delta_0) = \Delta_0;$$

$$\varphi(\omega) = \int_{\Delta_0}^{\omega_C} \mathrm{Re}\frac{\Delta(\nu)}{(\nu^2-\Delta^2(\nu))^{1/2}}d\nu \int g(\Omega)O^+(\nu,\Omega,\omega)\,d\Omega - U(\omega_C),$$

$$Z(\omega) = 1 - \frac{1}{\omega}\int_{\Delta_0} \mathrm{Re}\frac{\nu}{(\nu^2-\Delta^2(\nu))^{1/2}}d\nu \int g(\Omega)O^-(\nu,\Omega,\omega)\,d\Omega,$$

$$O^\pm = \frac{1}{\nu+\Omega+\omega+i\delta} \pm \frac{1}{\nu+\Omega-\omega-i\delta},$$

$$g(\Omega) = \alpha^2(\Omega)F(\Omega), \qquad F(\Omega) = \int d^3q\,\delta(\Omega-\Omega_q), \qquad (3)$$

where $F(\Omega)$ and q are the density and momentum of states of lattice oscillations, $\alpha(\Omega)$ is the effective function of electron-phonon interaction, $U(\omega_C)$ is a term which takes the Coulomb interaction into account.

It is clear that by using the set of equations (3) and the experimentally determined dependence Re $\Delta^2(\omega)$, we can obtain information on the function $g(\omega)$ characterizing the distribution over the energy ω of the density of lattice oscillations and the electron-phonon interaction,[5,7] and can also establish the function $g(\omega)$ of the investigated superconductor.[8]

Finally, as follows from the research of Migdal,[9] through the value of $g(\omega)$ one can determine how the density of states, the velocity, the effective mass m_e of the electrons in the normal state all change as a result of electron-phonon interaction near the Fermi surface. For example, $m_e = m_0 Z_0$, where

$$Z_0 = 1 + 2\int d\omega\, g(\omega)/\omega. \qquad (4)$$

The following metals were chosen for the study: Bi, Ga, Al, In, Sn, and Pb. In low-temperature condensation of Bi and Ga, a new, unstable, apparently amorphous phase is formed.[10] For the other metals, only distortion of the crystalline structure takes place as the result of the low-temperature condensation. Preliminary results of our study were reported in[11-13].

An object of the study was the system $Al-Al_2O_3-Me$, where Me is the studied metal. The system was prepared in the glass apparatus shown in Fig. 1. Films were evaporated on the bottom of the cup 1. Electrical contact with the films was made through the platinum contacts 2, applied by means of cathode sputtering, and platinum leads sealed through the glass, 3. The form of

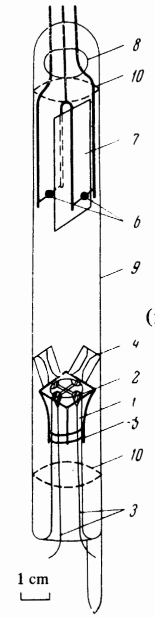

FIG. 1. Apparatus for preparation of tunnel systems (notation described in text).

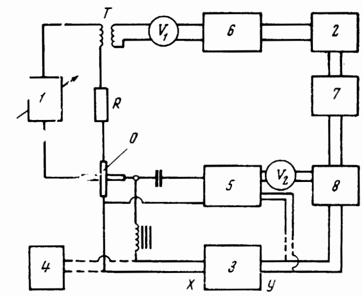

FIG. 2. Arrangement for measurement of junction characteristics: O – sample, 1 – source of smoothly changing, constant voltage V = +10 – –10 V with development time 1–16 min; R – resistor limiting the current through the junction ($R \gg R_{junc}$); 2 – source of sinusoidal oscillations (3G-10); 3 – x-y recorder; 4 – constant current potentiometer; 5 – resonance amplifier; 6 – filter of second harmonic generator (~ 3 × 10^{-3}); 7 – frequency doubler, used in recording d^2V/dI^2; 8 – synchronous detector. Operating frequency of amplifier 284 Hz, generator frequency in recording dV/dI- and d^2V/dI^2 characteristics 284 and 142 Hz, respectively.

the films was determined by the movable screens 4, attached to the cup by means of wire 5. Evaporation of the metal was effected from tungsten spirals previously heated 6; the screen 7 protected the evaporators from mutual contamination. The glass insulator 8 served to reinforce the evaporators.

The preparation of the sample was carried out in the following manner. The assembly was heated at ~500°K under pumping to 10^{-6} torr. Then, an aluminum layer was deposited at 300°K. Well dried air was brought into the apparatus at 400 torr and oxidation of the aluminum took place at 500°K with formation of a layer of Al_2O_3. The oxidation time was varied from 2 to 12 hours, depending on the metal studied. After oxidation, the apparatus was evacuated and sealed off. In the time of evaporation of the metal, the apparatus was immersed as a whole in liquid helium which was at a temperature below 2°K.

After carrying out all the measurements, the external jacket of the apparatus 9 was cut open along the place marked by the dashed curve 10. After necessary measurements, replacement of the evaporators, cleaning and application of the platinum contacts, the setup was restored. By changing the pressure above the liquid helium in the helium bath, it was possible to carry out measurements on the apparatus in the temperature range 1–4.2°K. To obtain higher temperatures, the method of "inverted dewar" was used.[14] For this purpose, a miniature heater and a carbon resistance thermometer were placed in the cavity of the cup 1. By changing the power dissipated in the heater, it was possible to carry out measurements in the range 4.2–30°K in the apparatus while it was wholly immersed in the liquid helium.

During the course of the experiment, I, dV/dI and d^2V/dI^2 were recorded as functions of V. For measurement of the dV/dI- and d^2V/dI^2-characteristics, a modulation method was used. Figure 2 shows the schematic diagram. For measurements of dV/dI, a modulated signal was used on the sample, equal to 1–10 μV, in

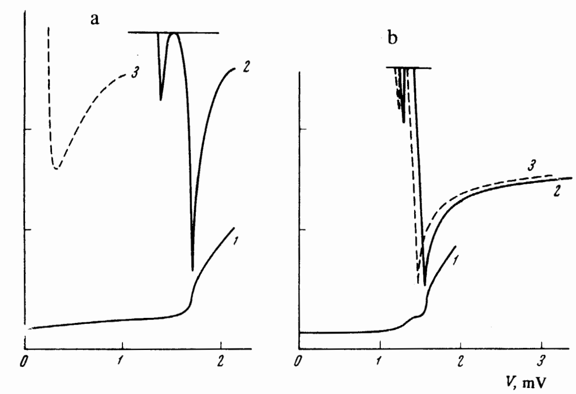

FIG. 3. Dependence of I and dV/dI on V for the samples: a – Ga, b – Pb. Curves 1 – I(V), 2 – dV/dI at 1°K for samples condensed at 1.6°K, curves 3 – dV/dI for the same sample after annealing to 300°K.

measurements of d^2V/dI^2 it was equal to 50–200 μV; usually, the measurements were made for several values of the signal.

The width of the gap in the energy spectrum of the electrons was computed from the curves I(V) and dV/dI = f(V) similar to those shown in Fig. 3, on which were clearly marked singularities for $eV = \Delta^0_{Me} \pm \Delta_{Al}$, where Δ^0_{Me} is the gap width of the metal studied. The values of Δ_0 obtained are given in the Table. In the same Table are given the values of $2\Delta_0/kT_c$. The value of T_c was determined from the temperature of disappearance of the resistance or the appearance of a maximum for V = 0 in the dV/dI-characteristics of the junctions associated with the appearance of the gap in the energy spectrum of the electrons. As is seen from the Table, condensation of the metal at helium temperatures produces an increase not only in Δ_0 but also in the ratio $2\Delta_0/kT_c$.

In addition to those considered above, singularities at $eV > \Delta_0$ were also observed in the characteristics of all the systems studied. These singularities were clearly established either by the dV/dI- or the d^2V/dI^2-

Characteristics of superconductors condensed at 2°K

Metal	T_c, °K	Δ_0, meV	$\frac{2\Delta_0}{\kappa T_c}$	Energy in meV of the singularities of g (ω)			
				main maximum of ω_0	additional maximum	end of spectrum	Z_0
Bi	6 (< 10^{-3})	1.185	4.6 [4.5 — 4.3]	3—3.5	8.5	12	3.7
Ga	8.4 (1.08)	1.156	4.25 (3.5) [4.3]	5	18	25	2.4
Pb	7.2 (7.2)	1.41 (1.36)	4.5 (4.3) [4.5]	4.5	8.5	10	3.8 (2.3)
Sn	4.2 (3.7)	0.75 (0.56)	4.05 (3.5) [4.0 — 3.9]	3.5—4	14	17.5	2.6 (1.6)
In	4.2 — 3.8 (3.4)	0.85 — 0.65	4.4 — 3.8 (3.45)		13.5	16	
Al	3 — 3.6 (1.16)	0.5	3.6 (3.35)		~30	40	

Note: In the curved brackets are given the characteristics of metals obtained under normal conditions; in the square brackets, values computed by the relation (9); two values correspond to possible change of ω_0. For In and Al, changes in the characteristic with thickness of sample are shown.

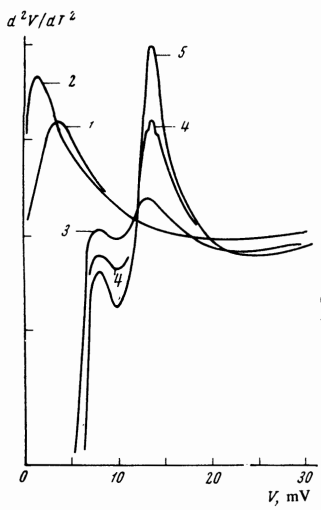

FIG. 4. Copy of recording of d^2V/dI^2 for Bi at various temperatures: 1–8, 2–6.5, 3–4.7, 4–42.5–1°K.

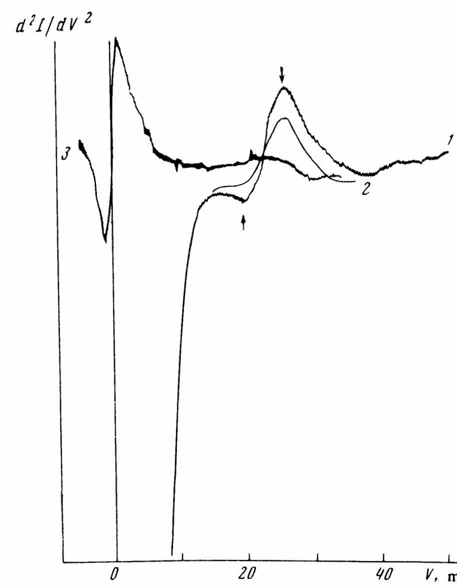

FIG. 5. Copy of recording of d^2V/dI^2 for Ga at various temperatures: 1 – 1.8, 2 – 4.2, 3 – 9°K.

characteristics of the junctions. They appeared on the curves $d^2V/dI^2 = f(V)$ in the form of maxima and minima, the location of which was practically temperature independent. The amplitude of these singularities gradually decreased for increase in the temperature to T_c, where they disappeared (Figs. 4 and 5).

Singularities were observed in the characteristics of the individual transitions which changed their position on the V axis, shifting to V = 0 upon increase in the temperature. Evidently, these singularities are connected with the disruption of the superconductivity of some elements of the system by the measuring current. Systems with such characteristics were not considered in the research.

From data similar to those in Figs. 4 and 5, the values

$$n(V) = \left(\frac{dV}{dI}\right)_n \Big/ \left(\frac{dV}{dI}\right)_s - 1,$$

$$n'(V) = \frac{dn}{dV} \approx \left(\frac{d^2I}{dV^2}\right)_s - \left(\frac{d^2I}{dV^2}\right)_n. \tag{5}$$

were calculated for all the metals studied.

If we assume that the change of dV/dI in the normal state is associated, for example, with the dependence of the transmissivity of the voltage barrier, which is not changed in the transition of the metal from the normal to the superconducting state, then the quantities n(V) and n′(V) will reflect the singularities of the tunnel characteristics, associated only with the superconductivity of the investigated metal.

Change of dV/dI with change in V in the normal state can be described completely satisfactorily for eV > 3kT by the following relation:

$$(dV/dI)_n = A[1 - \alpha \ln V], \tag{6}$$

where $\alpha \approx 10^{-2}$ for all the studied metals condensed at helium temperatures (V in millivolts). In the case of Bi, the transition of the sample to the nonsuperconducting modification is accompanied by increase in α (Fig. 6).

The appearance of a logarithmic maximum as V → 0, as in other similar cases (see [15]), can be due to the appearance of magnetic scattering at the barrier. The magnetic moments can in this case be connected with the unbound ions of oxygen in the barrier. The increase in the singularity in the transition of Bi to the nonsuperconducting modification can be connected with the change in the Fermi energy of the electrons which occurs in the transition.

Figures 7—9 give the dependence of n(V) and n′(V) for a series of investigated metals. In the region where $n < 2 \times 10^{-2}$, the curve n(V) is obtained by integration of

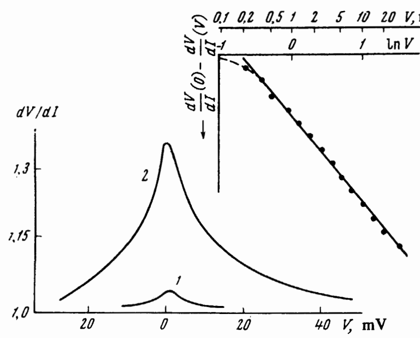

FIG. 6. Change of dV/dI with V in Bi in the normal state, T = 8°K. Curve 1 – sample condensed in helium; 2 – the same sample after annealing for 10 hours at 80°K. At the upper right, the same sample at 1°K; the voltage scale is logarithmic.

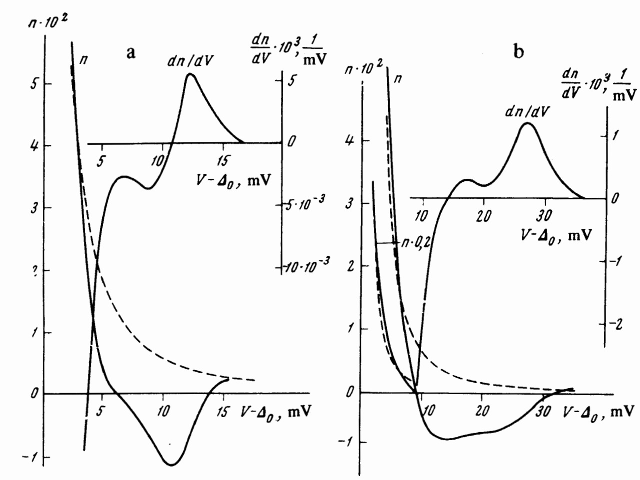

FIG. 7. Curves n(V) and n′(V): a – for Bi and b – for Ga, condensed at 2°K. Dashed curves – function n(V) according to BCS theory.

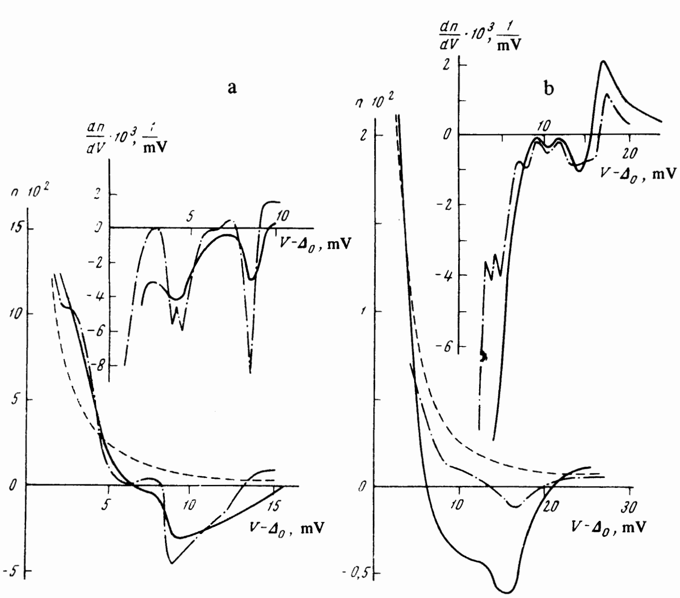

FIG. 8. Curves n(V) and n′(V) of samples: a – Pb and b – Sn, condensed at 2°K. Dot-dash curves – the same samples after annealing to 300°K. Dashed curves – function n (V) according to BCS theory.

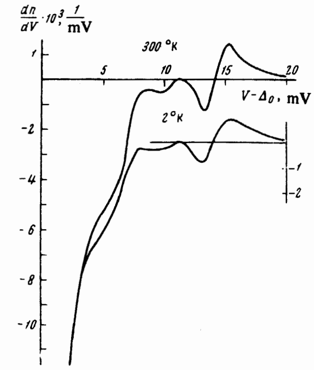

FIG. 9. Curves dn/dV as functions of $V - \Delta_0$ for In films of thickness 10^{-5} cm, condensed at 2°K and annealed at 300°K.

the curve $n'(V)$. Errors in the determination of $n'(V)$ can reach $2 \times 10^{-4}\ mV^{-1}$; moreover, a systematic error is possible in the value of $n = 0$ up to 3×10^{-3}. Curves obtained for different systems with the single metal (with the exception of In) are identical in the limits given above. In the case of In, a decrease in the thickness of the sample from 10^{-5} to 2×10^{-6} cm produces an increase of T_c to 4.3°K and of the ratio $2\Delta_0/kT$ to 4.4. Here $n(V)$ and $n'(V)$ change appreciably at the same time. The effect of increase of T_c with decrease in the thickness of the In films was discovered earlier in the work of Lazarev, Semenenko and Kuz'menko.[4]

Whereas at the beginning of the research, there were known only unsuccessful attempts to discover the singularities in the tunnel characteristics of the samples $n(V)$ and $n'(V)$, condensed at low temperatures, successful investigations have been carried out at the present time in a number of laboratories. Singularities in the characteristics for $eV > \Delta_0$ were discovered in Bi,[16] Ga,[17] and Sn.[18] In a series of researches, detailed measurements of Δ_0, T_c and $2\Delta_0/kT_c$ have been carried out (see, for example,[19]). The results of all these researches do not differ, within the limits of accuracy, from those given in the present work, only in the case of Ga, the values of Δ_0 and $2\Delta_0/kT_c$ in[16,19] exceed those obtained by us by ~5%.

Annealing of the systems studied by us leads to a

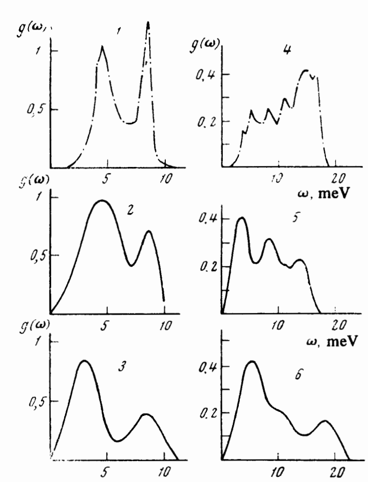

FIG. 10. Reduced functions g(ω) for Pb – curves 1, 2, Bi – curve 3, Sn – curves 4, 5, Ga – curve 6. Solid curve – sample condensed at 2°K, dot-dash curve, annealed sample.[8]

smooth transition of the characteristics to the form previously discovered in these metals, obtained under the usual conditions, singularities which it has been possible to connect with the appearance of a phonon spectrum.[8] Hence, we shall associate the singularities in the curves n(V) and n′(V) with the appearance of a spectrum of lattice oscillations of the metals that were condensed at helium temperatures.

The functions $g(\omega)$ were established from the curves n′(V) and n(V) with the help of the relations (3). The skepticism mentioned earlier by us regarding the possibility of application of the relations (3) to a metal with a nonideal lattice has proved to be excessive. The functions $g(\omega)$ obtained in first approximation are shown in Fig. 10. The values of Z_0 are given in the Table. The relative error in $g(\omega)$ and Z_0 (see (4)) can reach 10–15%. For the annealed samples, the curves were identical with those published previously in[8].

It is seen from Fig. 10 that the low-temperature condensation produces a change of $g(\omega)$ in two directions. First, an appreciable smearing out takes place in the singularities of the curve $g(\omega)$ and only a single clear maximum remains on the curve n′(V), corresponding to the end of the spectrum of lattice oscillations. Second, a significant increase in $g(\omega)$ takes place in the region of small energies and smearing out of the corresponding maximum down to $\omega = 0$. Absence of a distinct minimum in the curve n′(V) in the region of the smallest maximum of $g(\omega)$ is connected with such a circumstance.

So far as is known (see the discussion of[13]), independently of our calculations of $g(\omega)$ for Bi, it has also been established that $g(\omega)$ begins practically from $\omega = 0$. Moreover, the authors confirm the fact that $g(\omega)$ is proportional to ω at low energies.

The singular dependence of $g(\omega)$, discovered for metals with a crystalline lattice extremely distorted as a consequence of condensation at low temperatures, makes it possible both to explain a number of their superconducting properties, and also to express certain assumptions on the singularities of their properties in the normal state.

As is seen from the relations (3), the gap width Δ_0 is used in the operation of establishing $g(\omega)$. By the same token it is obvious that, within the framework of the theory, which describes the electron-phonon interaction, increase in the gap width, and correspondingly, T_c is explained in natural fashion by the change in $g(\omega)$. This change of $g(\omega)$ consists principally of a displacement of the center of gravity of the entire curve g in the region of low energies. At first glance, it appears that this result is in contradiction with the known formula of the BCS theory, according to which

$$T_c \sim \langle\omega\rangle e^{-1/NW}, \tag{7}$$

where $\langle\omega\rangle$ is the characteristic frequency of the spectrum of lattice oscillations, N the density of electron states near the Fermi surface, W the constant of electron-phonon interaction. Actually, increase in $g(\omega)$ in the low energy region indicates a decrease in the mean characteristic frequency of lattice oscillations which, in accord with (7), should give rise not to an increase, but to a decrease in T_c. This apparent contradiction is connected with the fact that in actuality, Eq. (7) is very approximate and in explicit form it does not take into account the dependence of the terms in the exponent on $\langle\omega\rangle$, for example, the change in W, N as a result of the electron-phonon interaction. Approximate account of this effect leads to the following expression:[20]

$$T_c \sim \langle\omega\rangle \exp(-\beta\langle\omega\rangle^2),$$

from which it is seen that a decrease in $\langle\omega\rangle$ actually produces an increase in T_c.

Let us write down one more approximate expression for the gap width in terms of Z_0:[19]

$$T_c \sim \Delta_0 \sim \langle\omega\rangle \exp\left\{-\frac{Z_0}{Z_0-1}\right\} \tag{8}$$

from which it can easily be seen that an increase in Z_0 ought to lead to a rise in T_c. Here the relative effect will be the greater, the smaller the ratio $T_c/\langle\omega\rangle$. From this viewpoint, the results of Buckel and Hilsch[2] on the connection of the relative increase of T_c and the ratio T_c/Θ_D become very clear. Since the dependence $T_c(Z_0)$ has a broad maximum near $Z_0 \sim 3$ ($Z_0 - 1 \approx \langle\omega\rangle^{-2}$), it is difficult to expect an appreciable increase in T_c or Δ_0 for superconductors with large values of Z_0 (Hg, Pb). Finally, none of these estimates should be taken too seriously, since they are based on approximate relations.

A change in the form of $g(\omega)$ and the shift of the maximum to the low energy region should lead also to a change in the ratio $2\Delta_0/kT_c$ (since this quantity depends on T_c/Θ_D). For this purpose, it is most convenient to use the relation obtained by Geĭlikman and Kresin:[21]

$$\frac{2\Delta_0}{kT_c} = 3.52\left[1 + 5.3\left(\frac{T_c}{\omega_0}\right)^2 \ln\frac{\omega_0}{T_c}\right]; \tag{9}$$

Here ω_0 is the frequency corresponding to the principal maximum of $g(\omega)$. Substituting the value of ω_0 in (5), we obtain $2\Delta_0/kT_c$, in satisfactory agreement with the data obtained as the result of direct measurements (see the Table).

Thus, by assuming that the above mentioned change of $g(\omega)$ takes place as the result of low-temperature condensation, it is possible to explain the entire set of experimental data on the superconducting properties of metals condensed at low temperatures, all in terms of the modern theory of superconductivity. Unfortunately, it is not possible at the present time to show unambiguously which mechanism is associated with the change of $g(\omega)$. We assume that the principal role is played by the change in the lattice oscillation distribution density, for example, due to the appearance of additional modes of oscillation near lattice defects.

It is obvious that a change in $g(\omega)$ develops in the properties of the normal state of the metal, associated with the electron-phonon interaction. For example, for samples of Pb and Bi obtained by low-temperature condensation, the effective mass of the electrons m_e should differ by a factor of more than 3 from the mass of the free electron, since $m_e = m_0 Z_0$. Of course, most interest attaches to experiments on the study of properties associated with the spectrum of lattice oscillations as a result of which there is hope of explaining the reasons for a change in $g(\omega)$.

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