

of the "hot" phonons, to this end we write down the  $\sigma$ -factor of the "bottleneck" [4, 5] in the form

$$\sigma = \frac{\tau_{ph} v^3 c}{4\pi \nu^2 \Delta \nu T_1} \operatorname{th}^2\left(\frac{h\nu}{2kT}\right).$$

Here  $v = 4.2 \times 10^5$  cm/sec is the velocity of the longitudinal oscillations;  $c = 1.6 \times 10^{21}$  cm<sup>-3</sup> is the concentration of the paramagnetic particles;  $\nu = 14.2$  GHz is the frequency of the resonant phonons;  $\Delta \nu = 400$  MHz is the spectral width of the band of the "hot" phonons, assumed equal to the width of the EPR line;  $T = 1.5^\circ\text{K}$  is the temperature of the thermostat;  $\tau_{ph} = \ell/2v = 8 \times 10^{-7}$  sec is the phonon relaxation time and is determined by the sample dimension  $\ell$ ;  $T_1 < 3 \times 10^{-2}$  sec is the time of the direct spin-lattice relaxation via the longitudinal phonons in the absence of the "bottleneck"<sup>1)</sup>. The foregoing values yield  $\sigma > 160$ .

The temperature of the "hot" phonons  $T_{ph}$  is connected with  $\sigma$  by the relation [5]

$$T_{ph} = T/2 \{ (1-s) + [(1+s)^2 + 4\sigma s]^{1/2} \},$$

where  $s$  is the EPR line saturation factor, equal to approximately 10 under the conditions of the experiment. From this we get  $T_{ph} > 50^\circ\text{K}$ , which is in full agreement with the experimentally registered value  $100^\circ\text{K}$ .

In conclusion, the authors thank Professor I. L. Fabelinskii for valuable consultations.

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#### THICKNESS DEPENDENCE OF THE CRITICAL TEMPERATURE OF THE SUPERCONDUCTING TRANSITION OF COLD-DEPOSITED BERYLLIUM FILMS

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We have investigated the dependence of the critical temperature  $T_c$  of the superconducting transition on the thickness of beryllium films condensed at liquid-helium temperature; the superconductivity of these films was first observed by Lazarev, Semenenko, and Sudovtsev [1].

The films were prepared by thermal evaporation of small batches of metal (having a resistance ratio of about 200) from molybdenum and tungsten evaporators, unto the surface of a freshly-cleaved mica plate (in thermal contact with the glass "finger" of an ampoule immersed in liquid helium).

<sup>1)</sup>

The estimate of  $T_1$  was obtained from the experimentally determined [5] upper limit of  $T_1$  with allowance for the fact that in CeMn the velocities of the longitudinal and transverse waves are related like  $v_t/v_l \approx 0.6$ . We took into account here the dependence of  $T_1$  on the magnetic field, namely  $T_1 \sim \ell H^{-5}$  [6].

The film thickness was determined from the change of the frequency of a quartz plate located alongside the mica substrate at the same distance from the evaporator. The thickness measuring device was first calibrated with relatively thick tin films whose thickness was determined from the amplitude of the Mossbauer absorption, in analogy with the procedure used in [2]<sup>1)</sup>. The quartz resonator was prepared from a quartz plate measuring 10 x 12 x 0.4 mm, on which thin silver electrodes were deposited. The plate was secured in elastic phosphor bronze holder-contacts. The resonator was connected in the circuit of an oscillator based on a miniature dual-triode vacuum tube, operating at low temperatures in the immediate vicinity of the resonator. The oscillator frequency was measured with an electronic frequency meter. At a quartz-plate natural frequency  $\sim 10^6$  MHz, the change of the frequency for each 100 Å of the thickness of the beryllium film was 180 Hz.

The critical temperature was measured by determining the change of the self-induction of a flat coil placed directly over the film in the glass "finger" of the ampoule. The coil was connected in an AC bridge circuit, the output of which was connected through an amplifier to the y coordinate of an automatic x-y recorder (see Fig. 1). The bridge was fed with an alternating voltage of  $\sim 200$  kHz frequency. The use of a sensitive amplifier at the output of the bridge made it possible to work with a very small voltage level on the measuring coil (10 - 100  $\mu$ V). Experiments showed that there was no need to plot  $T_c$  against the supplied power and to extrapolate it to zero.

Since the critical temperatures of beryllium films lie in the 5 - 8°K range, the transition curves were plotted at a slow heating of the "finger" of the ampoule. Prior to pouring the helium, the "finger" was filled with liquid nitrogen, which solidified and served as "thermal block." The substrate temperature was measured with a carbon thermometer placed on the bottom of the "finger". The signal from the thermometer was fed to the x-coordinate of the recorder.

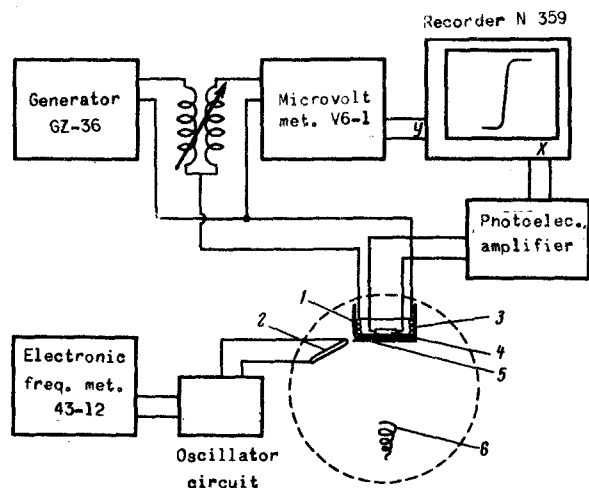


Fig. 1. Block diagram of setup for the measurement of  $T_c$ : 1 - glass finger, 2 - quartz plate, 3 - measuring coil, 4 - carbon thermometer, 5 - mica substrate, 6 - evaporator.

<sup>1)</sup> In the calibration of the thickness, the density of the cold-deposited beryllium was assumed equal to the density of hexagonal  $\alpha$ -beryllium, so that the thicknesses in Angstrom units are to some degree arbitrary.

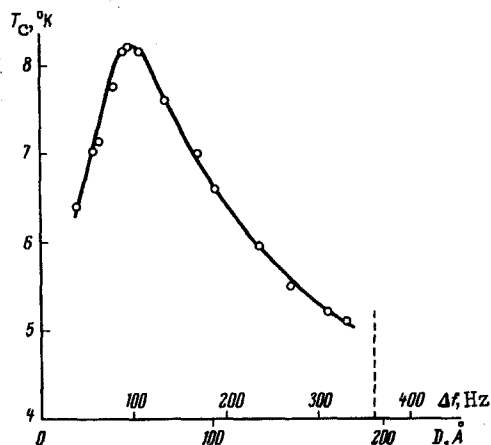


Fig. 2.  $T_c$  vs. thickness of cold-deposited Be films

We measured the critical temperatures of cold-deposited beryllium films in the range 25 - 1000 Å. The results are shown in Fig. 2. At thicknesses exceeding  $\sim 200$  Å, the films did not become superconducting down to 1.3°K. Thinner films revealed an approximately-exponential growth of the critical temperature with increasing thickness. The maximum critical temperature, 8.2°K, was observed for films  $\sim 60$  Å thick. With further decrease of the thickness, a drop of  $T_c$  was observed, and for a film  $\sim 25$  Å thick the value of  $T_c$  was 6.4°K.

The thickness dependence of  $T_c$  obtained for cold-deposited beryllium has the same appearance as the dependence obtained for aluminum films (cf., e.g., [3, 4]). It is not excluded that the causes leading to such a dependence are the same. Experiments on the absorption of monochromatic light [4] indicate that for Al films such a cause may be size quantization, which according to [5] should lead to a growth of  $T_c$  with decreasing thickness. It is very probable that the growth of  $T_c$  of Be films is also due to size quantization.

The decrease of  $T_c$  with thickness to the left of the maximum may be due to fluctuations, which, as is well known, cause  $T_c$  to vanish in the case of a monoatomic two-dimensional metallic layer [6]. This question is considered in detail in a paper of Kresin and Kogan. The decrease of  $T_c$  of films at very small thicknesses is a phenomenon common to all metallic films. Thus, for example, Fig. 3 shows the thickness dependence of  $T_c$  for cold-deposited tin films, measured by us by a similar procedure. According to the data of [7], a similar behavior is exhibited by films of Bi and Ga. A similar curve is shown for Pb in the review [8]. The absence of maxima for freshly-deposited films of these metals may be due to the fact that, unlike Al and Be, no size quantization takes place here, possibly because the surfaces of such films are less perfect. It must also be borne in mind that the small values of the carrier effective masses in Be greatly facilitate the appearance of size quantization.

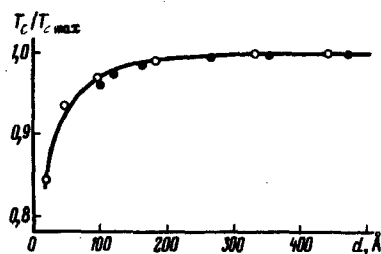


Fig. 3.  $T_c$  vs. thickness of cold-deposited Sn films. o - thickness determined with quartz thickness gauge, ● - thickness determined from amplitude of Mossbauer absorption (see [2])

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ELECTRON-VIBRATIONAL NATURE OF TWO-QUANTUM ABSORPTION IN CENTRALLY-SYMMETRICAL ORGANIC MOLECULES

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A large number of centrally symmetrical organic molecules in "violation" of the alternative forbiddenness reveal an intense two-quantum absorption in the region of allowed single-quantum transitions. Attempts to attribute this fact to accidental degeneracy [1] of the electronic states or to quadrupole and magnetic-dipole transitions [2] are unsuccessful, since the former explanation is not very likely (accidental degeneracy must be assumed for a larger number of molecules, and such a degeneracy contradicts the quantum chemical calculations), while the second does not yield the correct order of magnitude.

Recently, considerations were advanced [3, 4] explaining the presence of two-quantum transitions between electronic states of opposite parity as being due to the influence of molecule vibrations. When molecule vibrations are taken into account, the probability of the two quantum transition in the dipole approximation can be written in the form

$$W(\omega) = 4(2\pi)^3/\hbar^2 \sum_{i;k} \rho_{ii} \delta(\omega_{112k} - 2\omega) |M_{112k}|^2 \left(\frac{\omega F}{c n(\omega)}\right)^2 \delta F^2, \quad (1)$$

where  $n(\omega)$  is the refractive index,  $F$  is the quantum flux density,  $\rho_{ii}$  is the density matrix in the absence of the field and describes the distribution over the vibrational levels in the systems, and

$$M_{112k} = \sum_{m;j} \frac{d_{11m1} d_{mj2k}}{\omega - \omega_{mj2k}}, \quad (2)$$

where 1, m, and 2 are in turn the ground, intermediate, and final electronic states; i, j, and k are the vibrational sublevels of the corresponding electronic states, and  $\omega_{mj2k}$  are the frequencies of the transitions between the vibrational sublevels j and k of the electronic states m and 2.

We are interested here in the case of allowed single-quantum transitions in centrally symmetrical molecules. The states 1 and 2 have different parity. It is easy to verify that  $M$ , and with it  $\delta$ , are different from zero for a transition to the state 2 with excitation of odd harmonics of the asymmetrical vibrations (whereas the vibrational structure of the single-quantum transitions is determined by the even vibrational states).

Observation of the vibrational structure in the two-quantum absorption spectrum is an important argument in favor of its electron-vibrational nature. To reveal the vibrational structure, we investigated two-quantum absorption of anthracene dissolved in hexane, in the frequency range 13100 - 13800  $\text{cm}^{-1}$ . The tunable source was a laser operating on solutions of