

# INCREASE OF $T_c$ IN FINELY-DISPERSED TIN

I.G. Naumenko and V.I. Petinov  
 Institute of Chemical Physics, USSR Academy of Sciences  
 Submitted 2 March 1972  
 ZhETF Pis. Red. 15, No. 8, 464 - 467 (20 April 1972)

It is known that  $T_c$  increases in granulated tin. This is observed in thin films sputtered on dielectric substrates [1], and in tin granules imbedded in porous glasses [2]. A characteristic shortcoming of such samples is that it is very difficult to take into account the influence of the substrate on the increase of  $T_c$ . In addition, such samples are not convenient for the investigation of the influence of different dielectric coatings on the increase of  $T_c$ . The method of preparing granulated-tin samples by pressing finely-dispersed particles, which is used in the present investigation, is free to a considerable degree of the indicated shortcomings.

We investigated the influence of the particle dimension of finely-dispersed tin on the temperature of the superconducting transition. The investigations were performed with samples in the forms of disks of 8 mm diameter,  $\delta = 1$  mm, and prepared by pressing particles under a pressure of 8 kbar. The sample density did not exceed  $5 \text{ g/cm}^3$  (the density of tin is  $7.29 \text{ g/cm}^3$ ). The particles were obtained by an aerosol method [3]. The particle dimensions and their structure were determined with the aid of an electron microscope. The distribution of the particle dimensions was relatively small for each sample, as is typical of the aerosol method of obtaining particles [3]. The particles were spherical, and the structure corresponded to the  $\beta$ -tin lattice. The particles from the surface were oxidized in air. The degree of oxidation and the composition of the oxide were determined by the Mossbauer effect from the amount of absorbed oxygen.  $T_c$  was determined from the change of the resistance

and of the magnetic susceptibility of the samples. With increasing particle dimension and with increasing degree of their oxidation, the conductivity of the pressed samples became worse. For example, oxidation of the particles to a depth of two monolayers yields  $\sigma_{300^\circ\text{K}} = 10^3 \text{ ohm}^{-1}\text{cm}^{-1}$  for  $r_{av} = 500 \text{ \AA}$  and  $\sigma = 10^{-1} \text{ ohm}^{-1}\text{cm}^{-1}$  for  $r_{av} = 50 \text{ \AA}$ . The temperature dependence of  $\sigma$  was weak, but indicated that the conductivity was metallic.

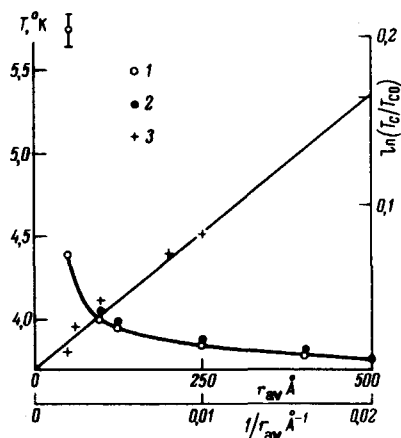


Fig. 1.  $T_c$  vs. the particle radius and  $\ln(T_c/T_{c0})$  vs.  $1/r_{av}$ : 1)  $T_c$  determined from the dependence of the magnetic susceptibility of the sample on  $T$ , 2)  $T_c$  determined from the dependence of the resistance on  $T$ , 3) dependence of  $\ln(T_c/T_{c0})$  on  $1/r_{av}$ .

Figure 1 shows experimental plots of  $T_c$  against  $r_{av}$  and of  $\ln(T_c/T_{c0})$  against  $1/r_{av}$ , for particles covered with two layers of oxide with  $T_c$  determined from the  $\chi(T)$  dependence (1) and  $T_c$  determined from the change of the sample resistance, when  $R = 0.5R_n$  (2). The width of the transition  $R/R_n$  was strongly dependent on the particle dimensions; it ranged from  $\Delta T \sim 0.11^\circ\text{K}$  for  $r_{av} = 500 \text{ \AA}$  to  $\Delta T \sim 3^\circ\text{K}$  for  $r_{av} = 50 \text{ \AA}$ . The value of  $T_c$  determined from the  $\chi(T)$  coincided, within the limits of experimental accuracy, with the

temperature at which the sample resistance vanished (see Fig. 2). To determine the influence of the oxide envelope of the particles on  $T_c$ , we performed measurements on samples with different degrees of particle oxidation. Figure 2 shows by way of an example plots of  $R/R_n$  and  $\chi(T)$  for samples with less than 5% oxidation (curves 1 and 1') and  $\sim 20\%$  oxidation (curves 2 and 2'). The average particle radius  $r_{av}$  was 100 Å. We see that the appearance of two monolayers of oxide leads to a noticeable increase of  $T_c$ .

Usually the increase of  $T_c$  in granulated superconductors is attributed to singularities in the phonon spectrum in small-dimension particles [2, 4]. In samples prepared by pressing finely-dispersed particles, the particles are in close contact with one another and it is therefore not very likely that the singularities of the phonon spectrum of the individual particles can become manifest in such systems.

It is of great interest to compare our experimental data with the conclusions of Ginzburg [5], who has proposed that the exciton mechanism of superconductivity comes into play in metal particles covered with a suitable dielectric. It follows from [5] that  $T_c$  of such systems can be estimated from the expression

$$\frac{T_c}{T_{c0}} \approx \left( \frac{\Theta_e}{\Theta_D} \right)^{g_b(1-\eta) + g_s\eta} \exp \left( \frac{(g_b - g_s)\eta}{g_b[g_b(1-\eta) + g_s\eta]} \right), \quad (1)$$

where  $\Theta_e = \hbar\Omega_e/k$ ,  $\eta = 3a/r$ ,  $g_b = n(0)|V_b|$ ,  $g_s = N(0)|V_s|$ ,  $T_{c0}$  is the critical temperature of the bulky superconductor,  $\Theta_D$  is the Debye temperature of the metal,  $\Omega_e$  is the characteristic frequency of the excitons in the dielectric,  $r$  is the particle radius,  $a$  is the layer of metal in which the influence of the dielectric penetrates,  $|V_b|$  and  $|V_s|$  are the effective potentials of the interaction in the metal and in the layer  $a$ , respectively, and  $N(0)$  is the density of states near the Fermi surface.

Making the perfectly reasonable assumptions  $\eta \ll 1$  and  $g_s \sim g_b$ , we can greatly simplify the expression (1):

$$\ln \left( \frac{T_c}{T_{c0}} \right) \approx \frac{3a}{r} \frac{g_s}{g_b} \ln \left( \frac{\Theta_e}{\Theta_D} \right). \quad (2)$$

Comparing (2) with the experimental dependence of  $\ln(T_c/T_{c0})$  on  $1/r_{av}$  (Fig. 1), we see that the experimental data agree qualitatively with the theory. If we assume that  $\hbar\Omega_e \sim 1$  eV and  $g_s \approx 1/4$  [6], then the slope of the line yields  $a \approx 1.5$  Å. In general, taking into account the approximate character of the calculations, we can expect the obtained value to be in agreement with the value  $a \lesssim 5 - 3$  Å given in [5]. One cannot, however, draw from the

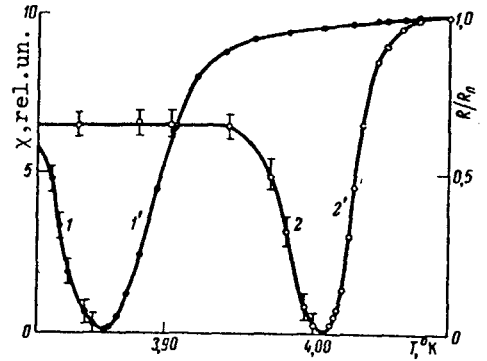


Fig. 2. Plots of  $R/R_n$  and  $\chi$  against  $T$  in the region of the superconducting transition for samples with different degrees of particle oxidation: 1, 1' - less than 5% oxidation, 2, 2' -  $\sim 20\%$  oxidation, 1', 2' -  $R/R_n$ , 1, 2 -  $\chi(T)$ .

foregoing the unequivocal conclusion that the increase of  $T_c$  in our samples is connected with the appearance of the exciton mechanism of superconductivity. To realize this superconductivity mechanism it is necessary that the dielectrics used to coat the particles have pronounced exciton bands lying much lower than the Fermi surface ( $\hbar\Omega_e \lesssim 1 - 2 \text{ eV}$ ) [5]. We do not know whether such exciton bands exist in tin oxide, which consists of  $\text{SnO}_2$  and  $\text{SnO}$ . In addition, the increase of  $T_c$  in our samples is possibly connected with the pairing of the conduction electrons on the particle surface as a result of the phonons of the dielectric [7]. In this case the relation (2) remains valid, except that  $\theta_e$  must be replaced by  $\theta_D$  of the dielectric (of the tin oxide).

In conclusion, we are sincerely grateful to A.D. Makrushin for investigating the degree of oxidation of the particles by the Mossbauer method, and also to V.T. Verkhovinin, A.S. Kovalev, and V.V. Shevchenko for help with the work.

- [1] B. Abeles, R.W. Cohen, and G.W. Cullen, Phys. Rev. Lett. 17, 632 (1966); V.M. Golyanov, A.P. Demidov, M.N. Mikheeva, and A.A. Teplov, Zh. Eksp. Teor. Fiz. 58, 528 (1970) [Sov. Phys.-JETP 31, 283 (1970)].
- [2] I.H.P. Watson, Phys. Rev. 2B, 1282 (1970).
- [3] M.Ya. Gen, M.S. Ziskin, and Yu.I. Petrov, Dokl. Akad. Nauk SSSR 127, 366 (1959); I.G. Naumenko, V.I. Petinov, and M.Ya. Gen, Fiz. Tverd. Tela 13, 3260 (1971) [Sov. Phys.-Solid State 13, 2740 (1972)].
- [4] I.W. Garland, K.H. Benneman, and F.M. Muller, Phys. Rev. Lett. 21, 1315 (1968).
- [5] V.L. Ginzburg, ZhETF Pis. Red. 14, 572 (1971) [JETP Lett. 14, 396 (1971)].
- [6] V.L. Ginzburg, Usp. Fiz. Nauk 101, 185 (1971) [Sov. Phys.-Usp. 13, 335 (1971)].
- [7] V.L. Ginzburg, Phys. Lett. 13, 101 (1964).

#### CONCERNING THE STRUCTURE OF NEODYMIUM LASER RADIATION

S.E. Potapov  
 S.I. Vavilov State Optical Institute  
 Submitted 6 March 1972  
 ZhETF Pis. Red. 15, No. 8, 467 - 471 (20 April 1972)

1. The inhomogeneously broadened luminescence band of  $\text{Nd}^{3+}$  in glass is usually represented as an aggregate of homogeneously broadened lines of Lorentz shape, corresponding to the emission spectra of the individual ions, between which nonradiative exchange (migration) of the excitation energy is possible. Such an idealization is convenient, but does not correspond to reality. We show in the present paper that in the case of monochromatically stimulated radiation the gain band becomes depleted not only within the limits of the homogeneous broadening near the radiation frequency, but also at a number of other frequencies. Such a frequency-selective coupling between parts of the luminescence is due apparently to the multicomponent structure of the working transition  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ , which is obscured by the inhomogeneous broadening. It can be assumed that the spontaneous structuring of the emission spectra in non-monochromatic quasistationary generation is due to a considerable degree to these effects.

2. The observation of the mutual relations between different parts of the gain band of the active medium was carried out in the following manner. Excitation of predominantly quasistationary generation at a preferred frequency  $\nu_0$  was stimulated for some time in a free running laser. The structure produced in the gain band was revealed by the appearance (or change) of the line structure excited in the generation spectrum far from the frequency  $\nu_0$ . The stimulated excitation was effected by a matched introduction of a radiation beam