Mössbauer effect in superconducting films of tin evaporated jointly with a tin complex of etioporphyrin

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We have investigated the Mössbauer effect on Sn^{119} nuclei in a tin complex of etioporphyrin and in superconducting films of tin evaporated jointly with this organic complex. It is shown that in such films, which constitute a finely dispersed granulated system of metallic particles in the matrix of the organic component, the Mössbauer absorption spectra of the organic complex differ from the absorption spectrum of the pure etioporphyrin complex. The main differences are the the weak temperaure dependence of the absorption probability and the decrease in the absorption linewidth of the organic component. An isotopic exchange is observed between the tin in the metallic granules and the tin in the etioporphyrin complex. No changes of the chemical shift were observed. The results confirm the previously advanced hypothesis that no interaction capable of greatly influencing the superconducting transition temperature of the system takes place between the tin granules and the organic complex.

In our earlier studies[1,2] we investigated the properties of metallic films (Be, Zn), evaporated jointly with the zinc etioporthyrin complex. The superconducting temperature of such films was as a rule 20–30% lower than the value T_c for the films without the etioporphyrin. The electric and optical data obtained in[1,2] indicate that these films constitute a finely-dispersed granulated system of metallic particles in the matrix of the organic component, and it appears that the possible interaction between the metal and the organic components does not take place. A small change of T_c can be due to the influence of the small dimensions of the granules on the electron and phonon spectra of the system. It was suggested in[1,2] that an energy barrier is produced on the metal—dielectric boundary and prevents the appearance of a coupling between the organic molecules and the metal.

It was of interest to study the features of metal films evaporated simultaneously with the organic dielectric, by measuring the resonant absorption of the γ quanta in the organic and metallic components of the film. To this end, we measured the Mössbauer effect on Sn^{119} nuclei in tin films evaporated jointly with the tin complex of etioporphyrin1). The measurements were performed with the setup described in[3]. The radiation source was Sn^*O_2. The absorption spectrum was plotted point by point by multiple passage through a fixed set of absorbable velocities. For ~1% absorption amplitudes, (1–2) $\times 10^6$ counts were accumulated for each point.

MÖSSBAUER EFFECT IN THE TIN COMPLEX OF ETIOPORPHYRIN

To measure the Mössbauer effect in pure tin complex of etioporphyrin (Sn-ep) we prepared absorbers in the form of thin pressed tablets of Sn-ep. The tin and the Sn-ep were of natural isotopic composition with Sn^{119} contents 8.56%. Figure 1 shows a series of the absorption spectra obtained at different temperatures for the Sn-ep sample, while Table I shows the principal parameters for these spectra, namely the absorption amplitude ϵ, the resonant velocity v_r, the line width Γ, and the area S under the absorption curve, calculated in units of the natural line width Γ_0, which amounts to 0.31 mm/sec for Sn^{119}. At all the temperatures, the absorption curves were strongly broadened and the shape of the curve differed strongly from Lorentzian, this probably the consequences of quadrupole splitting, The splitting ΔE was approximately equal to $3.5\Gamma_0$ (1.1 mm/sec) and decreased somewhat with rising temperature.

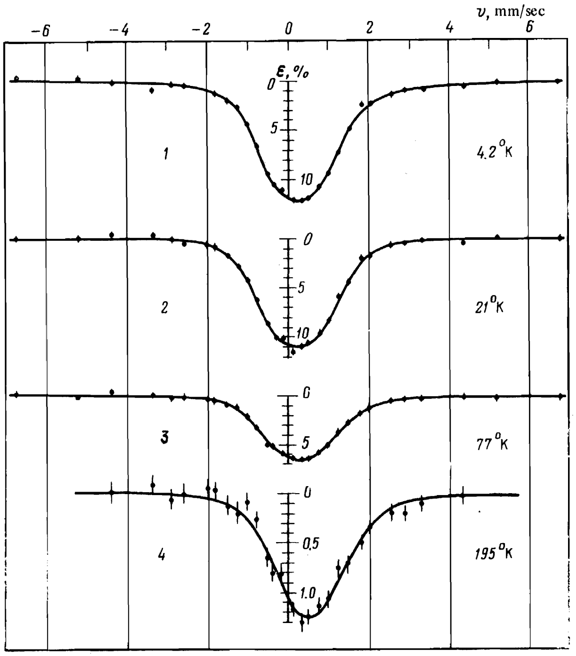

FIG. 1. Mössbauer absorption spectra of pure tin complex of etioporphyrin at various temperatures. The parameters of the spectra are given in Table I. The scale of curve 4 is magnified ten times.

A characteristic feature of the obtained data is the strong temperature dependence of the area S of the absorption curve, and consequently also of the probability f′ of recoilless absorption.

RESONANT ABSORPTION IN TIN FILMS EVAPORATED JOINTLY WITH THE TIN COMPLEX OF ETIOPORPHYRIN

The Sn + Sn-ep films were prepared by condensing both components on a mica substrate kept at liquid-helium temperature. The instrument in which the evaporation was carried out was described in detail

TABLE I

Curve 1 of Fig. 1	T, °K	ε, %	v_p, mm/sec	Γ, mm/sec	S
1	4.2	12.2±0.2	0.25±0,05	2.2±0.1	1.02±0.05
2	21	11.0±0.2	0.25±0.05	2,2±0.1	0.86±0.04
3	77	6.4±0.2	0.30±0.05	2.2±0.1	0.52±0.03
4	195	1.25±0.1	0.6±0.1	2.0±0.1	0.09±0.01
—	300	0.4±0.1	0.6±0.2	1.4±0.2	0.03±0.01

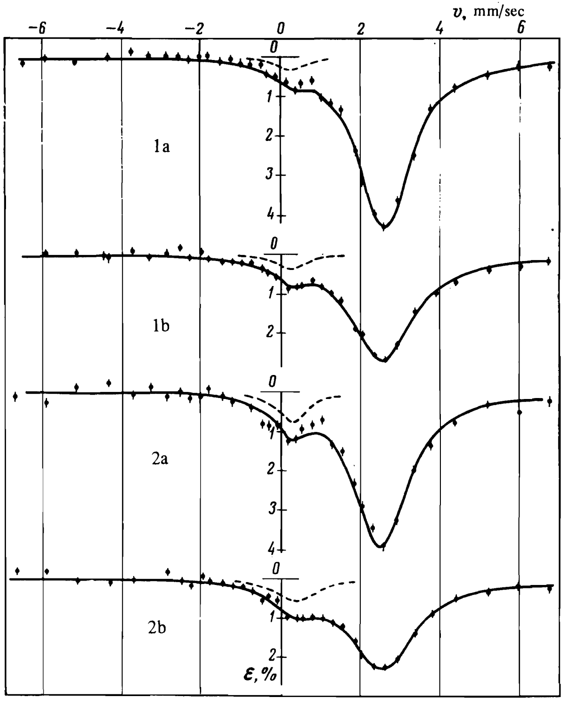

FIG. 2. Mössbauer absorption spectra of the system Sn + Sn-ep. Curves 1a and 1b were plotted a week after the preparation of the sample at temperatures 4.2 and 77°K, while curves 2a and 2b were plotted after a month, at the end of the measurement cycle. The parameters of the spectra are listed in Table II.

in[4]. The components were evaporated from two different evaporators, in analogy with the procedure used in[1,2]. The total thickness and the ratio of the components were monitored with a quartz meter. The tin was enriched with Sn^{119} to 88.7%. The Sn-ep contained, as before, the natural mixture of isotopes, with 8.56% Sn^{119}. To ensure a sufficient sensitivity relative to the organic component, we investigated films with relatively large concentration of the tin etioporphyrin. Just as in[1,2], the ratio of the organic and inorganic components was chosen to be approximately 1 : 3, and the layer thickness for the different samples was of the order of 150—500 A. To increase the effective thickness, a substrate with film measuring 20 × 20 mm was cut after preparation into four equal parts and gathered into a stack.

We measured the Mössbauer effect in the sample prepared in this manner at temperatures 4.2 and 77°K. The measurements were performed for a month in intervals of two or three days. In the time between measurements the samples were placed in the Mössbauer apparatus in a helium atmosphere at room temperature. Figure 2 shows the absorption curves obtained a week after the preparation of the sample, and after a month, at the end of the measurements[2]. It was impossible to resolve sufficiently well the absorption maximum of the organic component immediately after the preparation of the samples, owing to the small magnitude of the effect.

TABLE II

Curve 1 of Fig. 2	T, °K	ε, %	v_p, mm/sec	Γ, mm/sec	S
			Sn-etioporphyrin line		
1a	4,2	0.4±0.1	0.25±0.1	0.9±0.1	0.018±0.005
1b	77	0,4±0.1	0,25±0.1	0,9±0.1	0.018±0,005
2a	4.2	0.8±0.1	0.25±0.1	0.9±0.1	0.036±0.005
2b	77	0,6±0.1	0.35±0.1	1.2±0.1	0.036±0.005
			Tin line		
1a	4,2	4.3±0.1	2.6±0.05	1,65±0.1	0.36±0.02
1b	77	2,7±0.1	2.55±0.05	1.9±0,1	0.26±0.02
2a	4.2	3.9±0.1	2,50±0.05	1.65±0.1	0.325±0.02
2b	77	2.25±0.1	2,50±0.05	2.1±0.1	0.235±0.02

On the curves plotted a week after the preparation of the samples, one can see clearly two absorption maxima (see Fig. 2, 1a and 1b). The parameters of the spectra shown in Fig. 2, after resolving into components, are presented in Table II.

The principal results obtained with the system Sn + Sn-ep reduce to the following.

The position of the absorption line (the chemical shift) of the Sn-etioporphyrin in the Sn + Sn-ep system coincides with the position of the line in the pure Sn-ep complex.

The amplitude ε of the effect and the area S of the curve decrease in the course of time for the tin in the metallic granules, and increase accordingly for Sn-ep. This indicates that isotopic exchange takes place in the Sn + Sn-ep system between the tin granules and the tin contained in the etioporphyrin complex. Since the granules consist of metal enriched with Sn^{119}, while the tin in the Sn-ep is of natural isotopic composition, the increase of the effect in the Sn-ep is due to its enrichment with Sn^{119}.

The temperature dependence of the probability f′ for the absorption line of Sn-ep in the Sn + Sn + ep system turned out to be much smaller than for pure Sn-ep. This is clearly seen from a comparison of the absorption curves plotted at different temperatures at the end of the measurement cycle, when the etioporphyrin line no longer increases amplitude, i.e., after equilibrium has been established between the metallic tin and the tin in the Sn-ep. In this case the area of the absorption curve remains practically unchanged with increasing temperature from 4.2 to 77°K. For pure Sn-ep in the same temperature interval, S decreases to one-half (see Table I).

In addition, a sharp decrease of the line width Γ in the etioporphyrin is obtained in the Sn + Sn-ep in comparison with the absorption line width in the pure etioporphyrin. Whereas for pure Sn-ep at 4.2°K we have Γ = 2.2 mm/sec (see Table I), in the Sn + Sn-ep the width of the Sn-ep line is Γ = 0.9 mm/sec. Taking into account the magnitude of the quadrupole broadening in the source, one can conclude that within the limits of experimental error the Sn-ep line width coincides with the natural line width Γ_0. This circumstance can be regarded as an abrupt decrease of the gradient of the electric field at the tin nucleus in the Sn-ep complex.

It should be noted that the position of the Sn-ep line (v_r = 0.25 mm/sec) is very close to zero velocity, i.e., to the value of the chemical shift for tin dioxide. Therefore the appearance of a maximum near the origin and its increase with time could be ascribed to oxidation of the film granules. To exclude this possibility, control experiments were made on tin films evaporated jointly with the zinc etioporphyrin complex Zn-ep. Experiments performed for a month in analogy with the procedure described above have shown that the absorption spectrum has a single broadened line of metallic tin and does not change with time.

In addition, the width of the Sn-ep line in the Sn + Sn-ep system differs strongly from that of the oxide (the line is much broader before the oxide and the quadrupole broadening in SnO_2 amounts to 1.5 Γ_0). It must be emphasized that to exclude the possibility of oxidation, all the samples, including the control samples, were provided with an upper coating of etioporphyrin without the metal, H_2-ep.

With respect to the metallic-tin line in the Sn + Sn-ep system, it should be noted that it is greatly broadened, unlike the Sn-ep line, in comparison with the absorption line of a thin film of polycrystalline tin. For the metallic-tin line in the Sn + Sn-ep system we have $\Gamma = 1.65$ mm/sec at 4.2°K and 2.1 mm/sec at 77°K. The absorption line of the thin polycrystalline tin film, according to our data[5], has $\Gamma = 1.4$ mm/sec. A similar broadening of the metallic-tin line was observed also in control samples with the zinc etioporphyrin complex.

DISCUSSION OF RESULTS

As indicated above, measurements of the Mössbauer effect in pure Sn-ep reveal a strong temperature dependence of f'. This temperature dependence indicates that the spectrum of the oscillations of tin in Sn-ep lies in the lower frequency region. The Debye temperature estimated from the Debye-Waller factor is 80–90°K. The low Debye temperature characterizing the low endpoint frequency of the oscillations indicates that the bond of the tin atom in the Sn-ep molecule is much weaker than that of the Sn atom in the metallic tin.

The chemical shift determined by the density of the electrons at the tin nucleus shifts somewhat with increasing temperature in a positive direction towards the value of the shift for metallic tin. It is not excluded that this shift is the consequence of the weakening of the Sn-N bonds.

The Mössbauer spectrum of Sn-etioporphyrin in the Sn + Sn-ep system, which is a finely dispersed system of tin granules separated by etioporphyrin, differs from the Mössbauer spectrum of pure Sn-ep. The weak temperature dependence of f' for the Sn-ep line indicates a harder oscillation spectrum of the tin atom in the complex. The decrease of the Sn-ep line width indicates a strong decrease of the electric field gradient at the Sn nucleus in the Sn-ep complex. All this may be the consequence of the deformation of the Sn-ep molecules enclosed between the metallic granules.

The fact that the Mössbauer line of metallic tin in the Sn + Sn-ep system, as indicated above, is noticeably broadened in comparison with the line of a thin film of polycrystalline Sn also confirms the assumption that the Sn + Sn-ep layer is a mechanically stressed system. The consequence of these stresses is the increase of the electric field gradients at the tin nuclei and the metallic granules and a line broadening. In exactly the same manner, the line of the tin in the metallic granules was broadened in control samples in which the tin complex of etioporphyrin was replaced by the zinc complex.

The onset of stresses in the tin granules in the case of simultaneous evaporation of the tin and the Sn-ep complex may be due to the fact that the tin granules condensed on the cold surface can have a sufficiently large number of vacant places. It is probable that the presence of these vacant places causes a relatively intense isotopic exchange between the tin granules and the Sn-ep. The relative change of the absorption amplitudes ϵ and of the areas S of the absorption curves for the tin in the metallic granules and the tin in the Sn-ep with time, as indicated above, is a consequence of this isotopic exchange.

Since the temperature of the superconducting transition of freshly condensed Sn + Sn-ep layers, as measured by us, did not exceed the value of T_c for pure cold-condensed tin films ($T_c = 4.7$°K), it must be assumed that no interaction is produced in this case between the tin granules and the tin in the Sn-ep, probably as a result of the onset of the energy barrier. This barrier can be the result of the formation, on the granule boundary, of a doubly charged layer, similar to that occurring in colloidal systems. The appreciable decrease of the Sn-ep line width in the Sn + Sn-ep system and the practically unchanged value of the chemical shift in comparison with the pure Sn-ep also favors the assumption that the tin atoms in Sn-Sp-ep are weakly bound to the tin in the granules. The data obtained earlier[2] indicate that the optical absorption spectra obtained for etioporphyrin evaporated with the metal do not change, thus confirming the absence of an interaction between the metal granules and the etioporphyrin.

If we compare the results of the investigations of layers obtained by simultaneous evaporation of the metal and the organic dielectric with the results obtained for chalcogenides "wedged apart" either by metal or by an organic complex[6,7], then it is natural to conclude that in the latter case bonds seem to be produced between the chalcogenide and the wedging system and lead to an appreciable influence on the temperature of the superconducting transition of the system. It is not excluded that further study of the thin metal plus metal-organic complex layers and of wedged-apart chalcogenides will make it possible to find a way of obtaining systems in which there is no energy barrier between the metal and the organic complex.

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[1] The tin complex of etioporphyrin was prepared by E. I. Fillipovich, to whom the authors are sincerely grateful.

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