^{129}I MOSSBAUER STUDY OF THE ORGANIC SUPERCONDUCTOR β*—(BEDT—TTF)$_2$I$_3$

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In the early fifties London suggested a hypothesis that seemed fantastic: high temperature superconductivity can play a certain role in biological systems. But only in 1981 a small step in this direction was made — Bechgaard in Holland prepared his first ambient pressure *organic* superconductor. Another one was prepared in 1983 in the Institute of Chemical Physics of Ac. Sci. of the USSR. The latter has been investigated with the Mossbauer effect in ^{129}I and we present the results in this paper.

The base of the investigated system is the sulfurorganic molecule bisethylenedithiotetrathiafulvalene (ET). The (ET) is almost a plane molecule excepting the terminal ethylene groups, which have two different stable conformations forming an angle with the molecular plane. Oxidation of ET by iodine in nitrobenzene in certain conditions produce crystals of ion-radical salt with ET as the cations and I_3^- as the anions with the formula $(ET)_2I_3$.

We have prepared β—$(ET)_2{}^{129}I_3$ which is a superconductor with $T_c \sim 1{,}5$ K. The crystals of the β—phase are triclinic and constructed from stacks of ET cations linked in sheets by shortened S...S intermolecular contacts /1/. It is the ET sheets that are responsible for the conductivity in the system. The ET sheets are separated with sheets of symmetric I_3^- anions. An important feature of this structure is in the fact that the terminal atoms of the triiodide anion reside in a cavity created the hydrogen atoms of the —CH_2—CH_2-groups of ET, and the H...I interaction in the cavity realizes the charge transfer from the ET to I_3^- sheets and gives a tridimentionality. The value of the charge transfer is the main parameter determining the filling of the conduction band.

The ^{129}I Mossbauer experiments were performed in a standard transmission geometry with a real time doppler velocity calibration with ^{57}Fe metal. The experimental spectra were fitted with the superposition of two pure quadrupole subspectra of the $5/2^+ — 7/2^+$ transition at the transmission integral line form. In preparation of the Mossbauer absorber the material was ground with silica. Following the results of paper /2/ we believe, that such treatment stabilizes the metastable β*-phase ($T_c \sim 8$ K), which is just that Mossbauer results are concerned with.

The typical spectrum is presented in fig. and parameters of the spectra are in table 1.

Following the Daily and Townes treatment of quadrupole splitting /3/ and the calibraition of the isomer shift /4/ it is possible to calculate the populations of the valent $5p_x$,$5p_y$,$5p_z$ orbitals of the iodines in I_3^-. The results of such calculation in the assumption of pure p-bonding are presented in table 2.

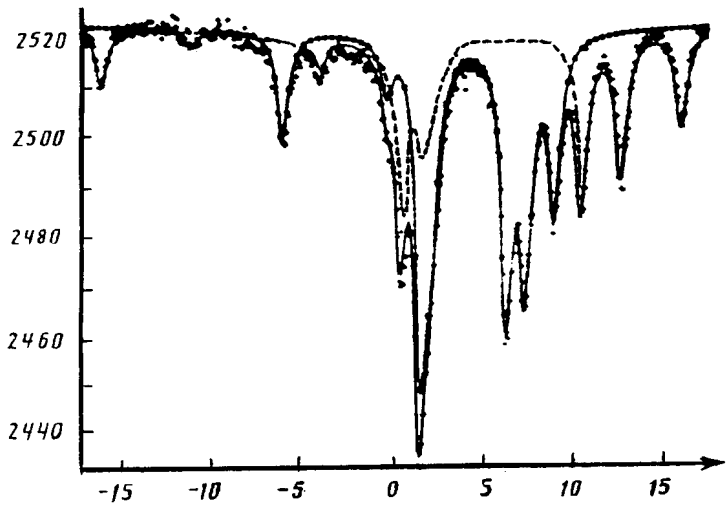

Fig.

Table 1

T_{abs}K		IS, mm/s	QS, MHz	η	I, %	Γ, mm/s
4.2	c	1.45(1)	—2468(5)	0	35.4(5)	0.83(5)
	t	0.21(1)	—1148(5)	0.04(1)	64.6(5)	
78	c	1.49(5)	—2504(15)	0	51(2)	1.63(9)
	t	0.38(5)	—1152(15)	0	49(2)	
140	c	1.9(7)	—2329(200)	0	55(20)	2.7(8)
	t	0.3(7)	—1117(250)	0	46(13)	

IS — isomer shift relative ZnTe source (mm/s), QS — $e^2q^{127}Q/h$ (MHz), I — relative area under subspectrum (%), η — asymmetry of EFG, Γ — line width (mm/s), «c» and «t» — central and terminal atom of I_3^-, respectively.

Table 2

Атом	N_x	N_y	N_z	q	Q
central	1.92(1)	1.92(1)	0.84(1)	0.32	—0.68
terminal	2.01(1)	1.99(1)	1.50(1)	—0.50	

$5p_x$, $5p_y$, $5p_z$ — populations of iodine atoms of I_3^- (N_x,N_y,N_z), atomic charge (q) and charge of I_3^- (Q).

The quantum chemical calculation of the charge distribution in the *isolated* I_3^- ion (supposing a full ion charge equal to —1) /5/ gives for the terminal atom charge —0.50 and for central one — zero. The experimental value for the terminal atom is in good agreement with the calculation, but it is not the case with the central one. The possible explanation here is in the polarization of I_3^- by the positively charged organic stacks. It should be mentioned that our experimental value for the full charge of I_3^- isn't the unity but 2/3, and this means that the charge transfer per single (ET) unit is $+1/3$.

An interesting feature of the system is the strong temperature dependence of the Mossbauer effect probability for the terminal atom in I_3^- (relative intensities, tab. 1). This is surprising because of the high coordination of the terminal atom. The dynamics of the I_3^- in this system should be studied more carefully.

In conclusion it should be noted that our results on the charge transfer and dynamics in this system in connection with the structural data on the terminal iodine surrounding /1/ make us suppose that the deuterium substitution for hydrogen in the ET molecule can give anomalously large isotopic effect on T_c.

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