Gamma-resonance studies of the organic superconductor β^*-$(\mathrm{ET})_2{}^{129}\mathrm{I}_3$

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Gamma-resonance spectroscopy of ^{128}I nuclei is used to study the electronic and dynamic characteristics of the tri-iodide anion in the organic superconductor β^*-$(\mathrm{ET})_2\mathrm{I}_3$. Signals are observed from two types of iodine atoms, i.e., the spectra correspond to a linear symmetric tri-iodide ion. An estimate, using the Townes-Daly model, of the electron-density distribution leads to a tri-iodide ion charge equal to -0.68; the terminal iodine atoms have in this case a charge -0.50, and the central one a charge $+0.32$.

INTRODUCTION

The first organic metals, such as TTF-TCNQ and its analog,[1] contained two systems of conducting "stacks," anions and cations. Their relative contributions to the conductivity and to other physical properties depended on the degree of charge transfer from cation to anion, a degree unknown beforehand; this made the interpretation of the experimental data highly complicated. Simpler in this respect are compounds with a single conducting system, such as the cation-radical salts TTT and TTF with inorganic anions, including the tri-iodide anion.[2-4] Total charge transfer was assumed to take place in them, and consequently the degree of filling of the conduction band was determined by the stoichiometric ratio of the cations and anions.

In the case of a tri-iodide anion containing ^{129}I, it is possible to determine by gamma-resonance spectroscopy not only the true charge of the anion, but also the orbital populations of the central and terminal iodine ions.[5] Five out of the ten presently known polyiodides *bis*(ethylenedithio)tetrathiofulvalene (ET) are superconductors,[6] viz. β-$(\mathrm{ET})_2\mathrm{I}_3$ ($T_c = 1.5$ K), β^*-$(\mathrm{ET})_2\mathrm{I}_3$ ($T_c = 8$ K), θ-$(\mathrm{ET})_2\mathrm{I}_3$ ($T_c = 3.5$ K), $\varkappa$-$(\mathrm{ET})_2\mathrm{I}_3$ ($T_c = 3.5$ K) and γ-$(\mathrm{ET})_2\mathrm{I}_{3.5}$ ($T_c = 2.5$ K). We report here the first results of gamma-resonance studies of the compound β^*-$(\mathrm{ET})_2\mathrm{I}_3$ which is the most fully investigated organic superconductor.

The crystal structure of this compound[7] consists of conducting planes of cation-radicals ET, separated by layers of linear centrosymmetric tri-iodide anions, so that the terminal iodine atoms are located in the voids between the hydrogen atoms of the ethylene groups of the ET molecules, while the distances between the iodine and hydrogen atoms are smaller than the sums of their Vander-Waals radii (Fig. 1). The compound β^*-$(\mathrm{ET})_2\mathrm{I}_3$ exists in two modifications (β and β^*) having $T_c = 1.5$ and 8 K respectively. In β-$(\mathrm{ET})_2\mathrm{I}_3$, one of the ethylene groups in the ET molecule is positionally disordered, and an incommensurate modulated superstructure appears below $T = 180$ K and leads to partial ordering of the ethylene groups. The ethylene groups in β^*-$(\mathrm{ET})_2\mathrm{I}_3$ are ordered and no superstructure transition takes place.

A study of the dynamics of the ethylene groups and of the associated dynamics of the tri-iodide anion, which can also be investigated by gamma-resonance spectroscopy, is of substantial interest.

EXPERIMENTAL RESULTS

The β-$(\mathrm{ET})_2{}^{129}\mathrm{I}_3$ crystals for the gamma-resonance investigations were obtained by oxidizing ET with iodine ($^{129}\mathrm{I}_3$) in nitrobenzene with a respective molar ratio 1:0.5. Two mixtures were synthesized at different cooling rates of the reacting solution after mixing the initial reagents at $t \approx 100$°C: $v_1 \approx 3$ deg/h (sample I) and $v_2 \approx 1.5$ deg/h (sample II). The conducting properties of the single crystals of these samples are different. Whereas samples I have $\rho_{300}/\rho_{4.2} = 300$ in the absence of a transition into the superconducting state all the way to 1.32 K, the crystals II are the better samples with ^{127}I, obtained by electrochemical and chemical oxidation of the ET (Fig. 2, curve 2) and have $\rho_{300}/\rho_{4.2} = 700$, $T_c = 1.5$ K. The x-ray structure parameters of the samples in both cases were identical and corresponded to β-$(\mathrm{ET})_2\mathrm{I}_3$. To prevent the possible texturing of the samples from affecting the gamma-resonance spectra (this could influence the relative intensities of the spectral lines), the samples were finely ground and mixed with finely powdered quartz glass, and then placed in hermetically sealed cells.

We have found that grinding the β-$(\mathrm{ET})_2\mathrm{I}_3$ sample to a powder causes it to become superconducting at $T_c = 7$–8 K. Figure 3 shows the temperature dependences of the para-

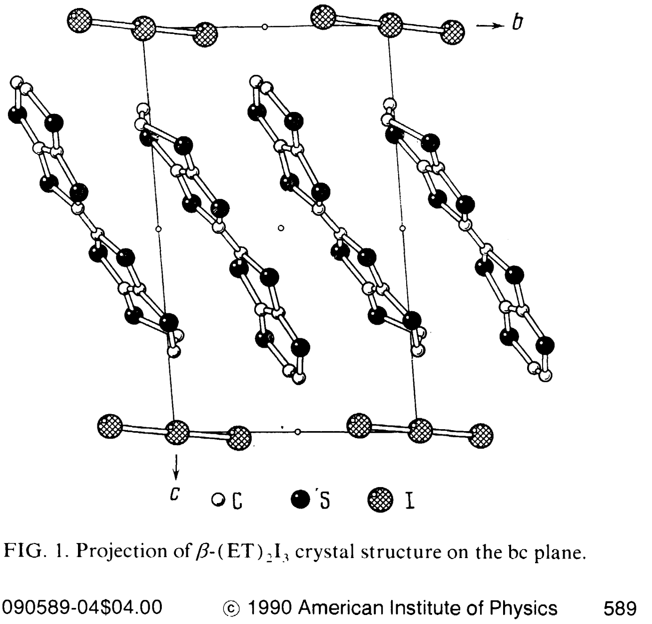

FIG. 1. Projection of β-$(\mathrm{ET})_2\mathrm{I}_3$ crystal structure on the bc plane.

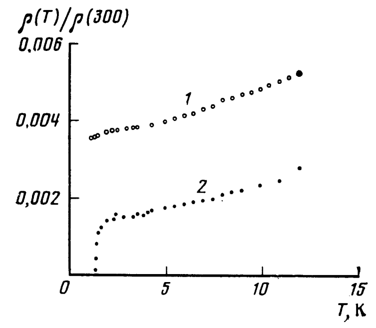

FIG. 2. Temperature dependence of normalized resistivity of β-$(ET)_2I_3$: 1—sample I, 2—sample II.

magnetic susceptibility χ_p of the $(ET)_2{}^{127}I_3$ sample, measured by the Faraday method in different states: curve 1—single-crystal sample (directly following the electrochemical synthesis); curve 2—in powdered form (the same crystals powdered in an agate mortar). We attribute this behavior difference between the crystal and the powder to stabilization of the β^*-$(ET)_2I_3$ state as a result of suppression of the superstructural transition after grinding up the sample, in view of the appearance of structure defects and twinning effects.[8]

The gamma-resonance spectra were obtained in standard transmission geometry with an immobile radiation source $5MgO\cdot{}^{129}TeO_3$ ($T_{1/2}\approx 33$ d) and a mobile investigated absorber. The spectra were reduced by least squares with the transmission integral calculated for a superposition of several quadrupole-split partial spectra, assuming a Lorentzian line shape. Each partial spectrum consists of eight resolved lines corresponding to transitions between the 5/2 and 7/2 multiplet levels of the ^{139}I nucleus. Figure 4 shows a typical gamma-resonance spectrum of ^{139}I in the compound β^*-$(ET)_2{}^{129}I_3$. The parameters of the partial spectra and the experimental conditions are listed in Table I. The same table shows for comparison some of the known parameters of the gamma-resonance spectra of other charge-transport complexes containing the linearly symmetric tri-iodide anion.

DISCUSSION OF RESULTS

We note first that the asymmetry parameters of the gamma resonance spectra of iodine atoms are close to zero, and there are only two nonequivalent positions of the iodine atoms in the system. This agrees with the x-ray structure data indicating that the tri-iodide anion in β-$(ET)_2I_3$ is symmetric and linear. The absence of a noticeable distribution of the parameters of the gamma-resonance spectra indicates that no modulated superstructure is observed, i.e., we are indeed dealing with β^*-$(ET)_2I_3$ samples. The populations N_i ($i = s, p_x, p_y, p_z$) of the $5s5p$-valence states of the iodine atoms in the tri-iodide anion were determined from the experimental data on the isomeric shifts δ, the quadrupole splittings e^2qQ, and the asymmetry parameters η, using the relations between these parameters and N_i on the basis of the Townes-Daly parameters[9]:

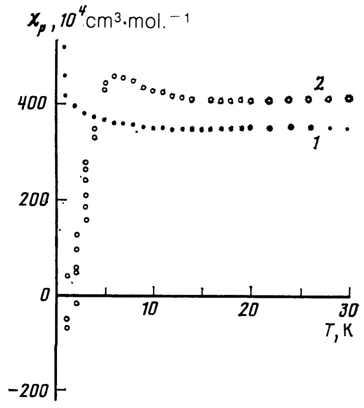

FIG. 3. Temperature dependence of paramagnetic part of the susceptibility of β-$(ET)_2I_3$: 1—initial single crystals, 2—after grinding to a powder.

$$\delta=-9(1)h_s+1{,}5h_p-0{,}54\ [\text{mm/s}]\ (\text{relative to ZnTe}), \qquad (1)$$

$$U_p=-N_{p_z}+(N_{p_x}+N_{p_y})/2=e^2q_{\text{mol}}(^{127}Q)/e^2q_{\text{at}}(^{127}Q), \qquad (2)$$

$$\eta=3|N_{p_x}-N_{p_y}|/2|U_p|, \qquad (3)$$

where

$$h_s=2-N_s, \qquad h_p=6-(N_{p_x}+N_{p_y}+N_{p_z}),$$

$$e^2q_{\text{at}}(^{127}Q)=2293\ \text{MHz}.$$

Since the population of the s state cannot exceed 2, it can be shown that Eqs. (1)-(3) (with allowance for the experimental data obtained for δ, e^2qQ, η and for their accuracy) are incompatible if $N_s < 2$, and have a common solution only if $N_s = 2$. This attests to the negligibly small participation of the s states in the hybridization of the valence orbitals of the iodine in the tri-iodide anion, in full accord with the known dependence of the degree of s–p hybridization on the difference between the ionization potentials of the s and p states. In this model we obtain effective charges -0.50 for the terminal atoms and -0.32 for the central one. The total charge of the tri-iodide anion turns out to differ substantially from -1 and equals -0.68 (Table II). Note that calculations of the charges of the iodine atoms of an isolated tri-iodide anion with charge -1 (e.g., in Ref. 10) lead to a terminal-atom charge -0.5 and a zero charge of the central atom I. The interaction of the terminal atoms of the iodine with the hydrogen atoms of the ethylene groups cannot fail to influence the distribution and magnitude of the excess negative charge of the tri-iodide anion. This is confirmed by the experimental data on δ, e^2qQ, η (Table I) for different compounds containing the tri-iodide anion, which confirm that its total charge differs from -1.

Note that the fact that the tri-iodide anion has a noninteger charge should have a number of exotic consequences. For example, the Fermi level should be located in this case inside an energy subband connected with the tri-iodide anion. Obviously, a large additional contribution, strongly dependent on the nature of the anion, should then be made to the density of states on the Fermi level. Yet the paramagnetic susceptibility of a number of isostructural ET complexes with linear anions are almost constant and not very large.[11]

Naturally, the foregoing model of calculating effective charges can be regarded only as a first approximation, since the Townes-Daly model does not take into account the lat-

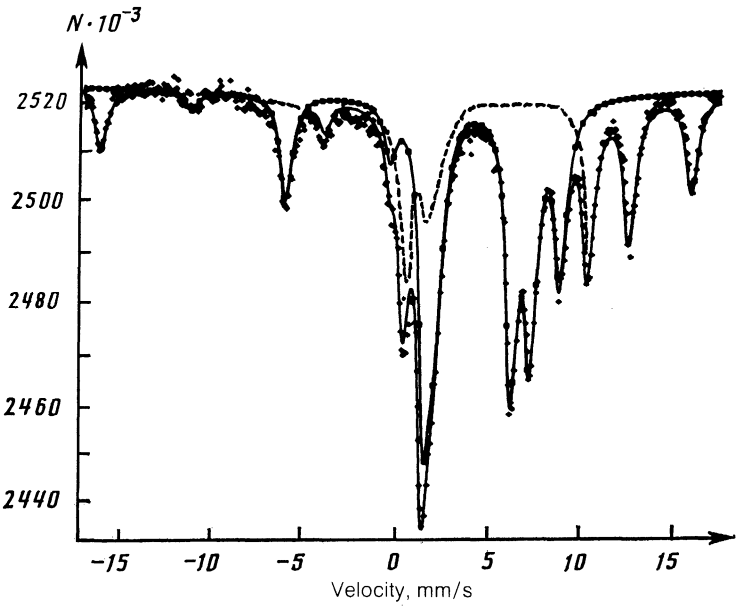

FIG. 4. Typical gamma-resonance spectrum of ^{129}I in the compound β*-$(ET)_2I_3$ and its resolution into components.

tice contribution to the electric-field gradient at the iodine nuclei in I_3^-.

It follows directly from the data of Table I that the ratio S_t/S_c of the areas of the partial spectra differs from 2 and depends on the temperature. This points to a rather large difference between the mean squares $\langle x^2\rangle$ of the oscillation amplitudes of the central and terminal iodine atoms in the tri-iodide ion at increased temperature. Such a behavior of the rms dynamic displacements of the iodine atoms seems to be a distinctive feature of the investigated system. Figure 5 shows the temperature dependence of the difference $\langle x^2\rangle_t - \langle x^2\rangle_c$ for sample I. Note that the abrupt decrease of the observed resonance absorption with increase of temperature makes impossible at present a sufficiently reliable interpretation of the small changes of the electronic states of the iodine atoms with rise of temperature, but the dynamic effect is manifested clearly enough. It appears that the rms displacements of the iodine atoms (terminal and central) corresponding to zero-point oscillations are also different.

Determination of the numerical values of $\langle x^2\rangle_t$ and $\langle x^2\rangle_c$, which is also made possible by analysis of the gamma-resonance spectra, calls for a special experiment. The $[\langle x^2\rangle_t - \langle x^2\rangle_c](T)$ dependence shown in Fig. 5, however, can be directly determined from the $S_t/S_c(T)$ dependence and requires no special experiments. To estimate $\langle x^2\rangle_c$ we can use, in first approximation, the data for the average frequency ω_c of the valance oscillations of the I—I bond and the Einstein model. Using the known expression

$$\langle x^2\rangle = \frac{\hbar}{M\omega}\,\mathrm{cth}\,\frac{\hbar\omega}{2kT} \tag{4}$$

and the value $\omega_c = 2\cdot 10^{13}\ \mathrm{s}^{-1}$ (Ref. 12) we obtain the $\langle x^2{}_c\rangle$ dependence. The experimental data on $[\langle x^2\rangle_t - \langle x^2\rangle_c](T)$ and the model data on $\langle x^2\rangle$ yield estimates of the quantities $\langle x^2\rangle_t(T)$ which are plotted in Figs. 5b and 5c. Using expression (4), we calculate the corresponding frequency ω_t, which turns out to be approximately half the value of ω_c. This does not contradict the structure of the tri-iodide anion and points to a weaker constant of the elastic coupling of the terminal iodine ions compared with the central one. The obtained estimates of $\langle x^2\rangle_t(T)$ and $\langle x^2\rangle_c(T)$ should be compared with the values determined directly from gamma-resonance spectra. Note that the oscil-

TABLE I.

Sample	T_{so}, K	T_{abs}, K	δ, mm/s	$e^2q^{127}Q/h$, MHz	η	S, %	Γ, mm/s
I	4.2	4.2	1.45(1)	−2468(5)	0	35.4(5)	0.63(2)
			0.21(1)	−1148(5)	0.04(1)	64.6(5)	0.63(2)
II	4.2	4.2	1.52(1)	−2510(5)	0	35.6(5)	0.63(2)
			0.26(1)	−1159(3)	0	64.4(5)	0.63(2)
I	78	78	1.49(5)	−2504(15)	0	51(2)	1.63(9)
			0.38(5)	−1152(15)	0	49(2)	1.63(9)
I	78	140	1.9(7)	−2329(200)	0	55(20)	2.7(8)
			0.3(7)	−1117(250)	0	46(13)	2.7(8)
[14]	4.2	4.2	1.48(5)	−2470(20)	0.06(4)	38(2)	–
			0.25(5)	−1115(20)	0.06(4)	62(3)	–
[15]	4.2	4.2	1.34(5)	−2381(15)	–	37(7)	–
			0.27(5)	−1231(15)	–	63(7)	–
[16]	4.2	4.2	1.38(4)	−2479(20)	–	–	–
			0.32(4)	−1235(20)	–	–	–

Remarks: The samples in Refs. 14, 15, and 16 are respectively $(Ru(Cp)_2I)I_3$, $NiPCI_{2.16}$ (where Pc is phthalocyanine), and $Cis(CHI_{0.02})_x$; T_{so}—radiation-source temperature, T_{abs}—absorber temperature, δ—shift relative to ZnTe.

TABLE II. Populations of valence states of iodine atoms in $^{129}I_3$ tri-iodide anion, calculated using Eqs. (1)-(3) with $N_\times = 2$.

Iodine atom	N_{p_x}	N_{p_y}	$'N_{p_z}$	$Z(I_i)$	$Z(I_c+2I_t)$
c	1.92(1)	1.92(1)	0.84(1)	0.32	−0.68
t	2.00(1)	1.98(1)	1.50(1)	−0.50	

Notation: c and t—central and terminal iodine atoms; $Z(I_i)$ and $Z(I_c+2I_t)$—charges on the I_i atom and on the I_3 anion, respectively; $i = c$ or t.

latory process that governs the rms displacements $\langle x^2\rangle_t(T)$ and $\langle x^2\rangle_c(T)$ has a period of order 10^{-12} s, much shorter than the characteristic time of the method (10^{-8} s).

We must dwell finally on the interpretation of the observed abrupt spectral-line broadening with rise of temperature. In contrast to $\langle x^2\rangle_{t,c}$, which are due to a purely oscillatory process, the broadening of the spectral lines is connected with stochastic motion processes, such as continuous or jumplike diffusion of the tri-iodide molecule as a whole.

The Mössbauer spectra were reduced in the present paper assuming a Lorentzian shape of the spectral lines. This question calls for refinement in view of the possible limited diffusion, and for introduction of appropriate corrections that can influence somewhat the quantative characteristics of the diffusion-discontinuity frequencies or the activation energies of the diffuse motions of the tri-iodide molecule in the surrounding hydrogen atoms of to various ethylene groups. Using the temperature dependence of the Mössbauer-spectrum linewidths and the expression for this width in the case of unbounded jumpwise diffusion[12]

$$\Delta\Gamma \approx \frac{2\hbar}{\tau_0}\exp\left(-\frac{E_a}{kT}\right), \qquad (5)$$

where τ_0 is the "settled" lifetime of the iodine atoms and E_a is the diffusion activation energy, we obtain $\tau_0 \approx 0.3\cdot 10^{-8}$ s and $E_a \approx 0.01$ eV. Such a relatively low activation energy is typical of conformational motions of ethylene groups in various molecular crystals, including apparently also ET. The line broadening observed in the Mössbauer spectra with rise of temperature is apparently due to diffuse jumps of the tri-iodide molecule as a whole, as a result of the freeing of the conformational motions of the ethylene groups and of the change of the character of the nearest surrounding of the terminal iodine atoms. Since these motions have low frequencies ($\sim 3\cdot 10^8$ Hz), it is not excluded that the line broadening is enhanced also by fluctuations of the electron environment. Note that at $T = 4.2$ K there is practically no spectral-line broadening. This means the absence of diffusion processes and high homogeneity of the electron environment the iodine nuclei (both terminal and central), and also of the crystal fields in the β^*-$(ET)_2I_3$ compound in the positions occupied by the iodine ions at $T = 4.2$ K.

We note in conclusion that our deduced fractional charge of the tri-iodide anion requires confirmation by other experiments. To cast light on this question it is necessary to investigate systematically organic metals based on ET (including poly-iodides) by gamma-resonance methods.

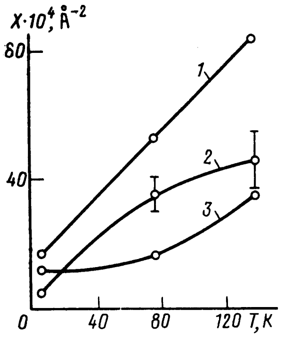

FIG. 5. Temperature dependences of the rms displacements of the terminal and central iodine atom and of their difference: 1—$X = \langle x^2\rangle_t$, 2—$X = [\langle x^2\rangle_t - \langle x^2\rangle_c]$, 3—$X = \langle x^2\rangle_c$.

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