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Influence of the Order–Disorder Transition in the Crystal Electron Subsystem on the Electron Density at Lattice Sites

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Abstract—The temperature dependence of the Mössbauer spectrum centroid S of $^{67}\text{Zn}^{2+}$ impurity atoms at the copper and yttrium sites of $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$, $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$, $\text{YBa}_2\text{Cu}_4\text{O}_8$, $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$, $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, $\text{HgBa}_2\text{CuO}_4$, $\text{HgBa}_2\text{CaCu}_2\text{O}_6$, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ compounds at temperatures $T > T_c$ (T_c is the superconducting transition temperature) is controlled by a second-order Doppler shift. The value of S in the temperature range $T < T_c$ is affected by the energy-band mechanism associated with the formation of Cooper pairs and their Bose condensation. A relationship between the electron density at the metal site of the crystal and its superconducting transition temperature is found. In the case of compounds containing two structurally nonequivalent sites for copper atoms, a change in the electron density caused by the Bose condensate of Cooper pairs is shown to be different for these sites. The experimental temperature dependence of the superconducting electron fraction conforms to a similar dependence following from the Bardeen–Cooper–Schrieffer theory for all the sites under study. © 2003 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

The superconducting transition of a crystal is a second-order phase transition. The Landau theory interprets it as a transition with a change in symmetry: at temperatures above the transition temperature T_c , the crystal electronic subsystem is characterized by a higher symmetry than at $T < T_c$ (the transition from Bloch wave functions of the metal to a single coherent wave function of the superconductor). Therefore, the electron density distribution at lattice sites of superconducting and normal phases should differ, and this difference can be measured using Mössbauer spectroscopy [1].

In this study, $^{67}\text{Cu}(^{67}\text{Zn})$ and $^{67}\text{Ga}(^{67}\text{Zn})$ emission Mössbauer spectroscopy was used to measure electron changes in density at copper and yttrium lattice sites of $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ ($T_c = 90$ K), $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$ ($T_c = 50$ K), and $\text{YBa}_2\text{Cu}_4\text{O}_8$ ($T_c = 80$ K) compounds during their superconducting transition. Copper atoms in the structure of these compounds occupy two structurally nonequivalent sites, Cu(1) and Cu(2) [2, 3]. It was not ruled out that the change in the electron density in these sites could be different. The change in the electron density was also studied in the copper lattice sites of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ ($T_c = 22$ K), $\text{La}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ ($T_c = 37$ K), $\text{HgBa}_2\text{CuO}_4$ ($T_c = 79$ K), $\text{HgBa}_2\text{CaCu}_2\text{O}_6$ ($T_c = 93$ K), $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ ($T_c = 80$ K), and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ ($T_c = 60$ K) compounds, where copper occupies a single site [4–6].

2. TECHNIQUE AND RESULTS

Mössbauer sources of superconducting samples were prepared by the diffusion of radioactive carrier-free ^{67}Cu and ^{67}Ga into polycrystalline compounds in evacuated quartz cells at 450°C for 2 h. As reference samples (in which a superconducting transition was not observed), we took materials produced by 2-h annealing of superconducting samples in air at 600°C . The Mössbauer spectra were measured with a ^{67}ZnS absorber. The absorber temperature was 10 ± 1 K, and the source temperature varied from 10 ± 2 to 90 ± 2 K.

The $^{67}\text{Cu}(^{67}\text{Zn})$ Mössbauer spectra of compounds characterized by single sites of copper atoms constituted quadrupole triplets; the spectra of compounds incorporating two copper sites represented a superposition of two quadrupole triplets.

The isomer shift ([I.S.]) in all of the spectra corresponds to $^{67}\text{Zn}^{2+}$ ions ([I.S.] ≈ 67 – 77 $\mu\text{m/s}$ with respect to the spectrum of the ^{67}Ga -in-copper source). Therefore, it was assumed that parent ^{67}Cu atoms occupy copper sites during diffusion doping; hence, the $^{67}\text{Zn}^{2+}$ probe produced after ^{67}Cu decay is at copper sites as well.

The $^{67}\text{Ga}(^{67}\text{Zn})$ Mössbauer spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$, $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$, $\text{YBa}_2\text{Cu}_4\text{O}_8$, and $\text{La}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ compounds represented quadrupole triplets whose [I.S.] corresponds to $^{67}\text{Zn}^{2+}$ ions ([I.S.] ≈ 100 – 107 $\mu\text{m/s}$). It was assumed that parent ^{67}Ga atoms occupy yttrium or lanthanum sites during diffusion doping; hence,

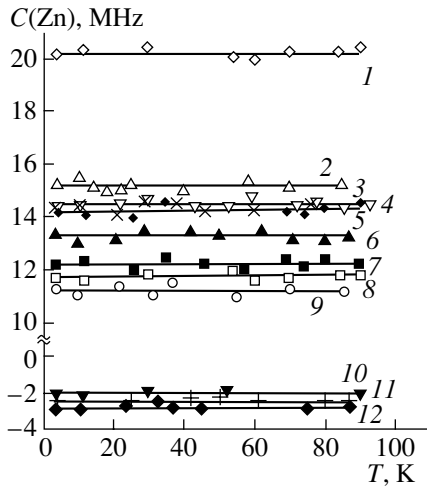


Fig. 1. Temperature dependences of the constants of the quadrupole interaction of $^{67}\text{Zn}^{2+}$ probe ions at the sites of (1) Cu(1) in $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$, (2) Cu in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$, (3) Cu in $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, (4) Cu(1) in $\text{YBa}_2\text{Cu}_4\text{O}_8$, (5) Cu in $\text{HgBa}_2\text{CaCu}_2\text{O}_6$, (6) Cu in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, (7) Cu(2) in $\text{YBa}_2\text{Cu}_4\text{O}_8$, (8) Cu(2) in $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$, (9) Cu in $\text{La}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$, (10) Y in $\text{YBa}_2\text{Cu}_4\text{O}_8$, (11) Y in $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$, and (12) Y in $\text{La}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$.

$^{67}\text{Zn}^{2+}$ probe atoms produced after ^{67}Ga decay are at corresponding sites as well.

The quadrupole interaction constants C for $^{67}\text{Zn}^{2+}$ centers in both copper and yttrium (lanthanum) sites are virtually independent of temperature (see Fig. 1). This is explained by the fact that the electric field gradient in ^{67}Zn nuclei for Zn^{2+} probe ions is preferentially caused by lattice ions, and the changes in the lattice constants of the compounds under study are very small in the temperatures range of 4.2–90 K [2–6].

3. DISCUSSION

The temperature dependence of the centroid S of the ^{67}Zn Mössbauer spectrum at a fixed pressure P is given by (see [7])

$$(\delta S/\delta T)_P = (\delta[\text{I.S.}]/\delta \ln V)_T (\delta \ln V/\delta T)_P + (\delta D/\delta T)_P + (\delta([\text{I.S.}])/\delta T)_V. \quad (1)$$

The first term on the right-hand side of expression (1) accounts for the dependence of the [I.S.] on the volume V ; it manifests itself at structural phase transitions. The second term represents the temperature dependence of the second-order Doppler shift D written in the Debye approximation as (see [7])

$$(\delta D/\delta T)_P = -(3k_0 E_0/2Mc^2)F(T/\theta), \quad (2)$$

where k_0 is the Boltzmann constant, E_0 is the isomeric transition energy, M is the probe nucleus mass, c is the speed of light in free space, θ is the Debye temperature, and $F(T/\theta)$ is the Debye function. Finally, the third term

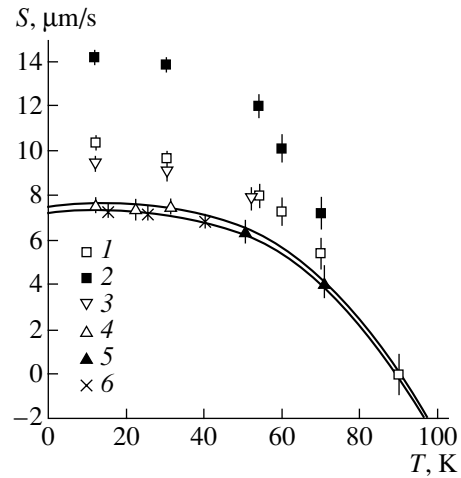


Fig. 2. Temperature dependences of the centroid S of the $^{67}\text{Zn}^{2+}$ Mössbauer spectra at the Cu(1) (1, 4), Cu(2) (2, 5), and Y (3, 6) sites measured with respect to their values at 90 K for $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ (1–3) and $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ (4–6). The solid line is the temperature dependence of S calculated for the second-order Doppler shift at $\theta = 420$ K.

in Eq. (1) describes the temperature dependence of the [I.S.]; it allows for a change in the electron density at Mössbauer nuclei, which is expected as the host converts to the superconducting state.

Typical dependences $S(T)$ for Cu(1), Cu(2), and Y sites in the $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ lattice are shown in Fig. 2. It turns out that the temperature dependence of the spectrum centroid S measured with respect to its value at T_c for reference samples is adequately described by formula (2) in the temperature range of 10–90 K if one uses the Debye temperatures determined from specific heat measurements [8–11]. In other words, the [I.S.] changes due to both volume and temperature changes almost have no effect on the dependence $S(T)$ for non-superconducting samples. Since there are no structural phase transitions for the compounds under study in the temperature range of 10–90 K, this $S(T)$ run is quite expected.

The dependence $S(T)$ at $T > T_c$ for all of the superconducting samples is also described by a second-order Doppler shift (see formula (2)), and the Debye temperatures remain unchanged in comparison with reference samples. In the temperature range $T < T_c$, the quantity S depends more heavily on temperature than follows from formula (2), and both the second and third terms should be taken into account in expression (1). The latter describes the temperature dependence of the [I.S.].

For quantitative determination of [I.S.], we introduce the following quantities.

(i) The isomer shift $[\text{I.S.}]_T$ at a given temperature T , which is defined as $[\text{I.S.}]_T = S_T - D_T$ (where S_T and D_T are the spectrum centroid and Doppler shift at the temperature T).

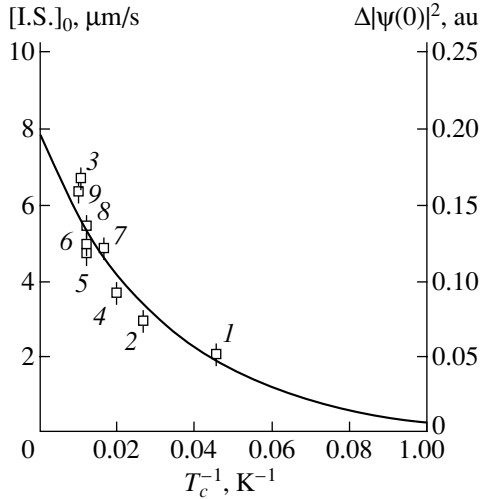


Fig. 3. Dependences of $[I.S.]_0$ and $\Delta|\Psi(0)|^2$ on T_c^{-1} . Squares are the data on (1) Cu in $Nd_{1.85}Ce_{0.15}CuO_4$, (2) Cu in $La_{1.85}Ce_{0.15}CuO_4$, (3) Cu(1) in $YBa_2Cu_3O_{6.9}$, (4) Cu(2) in $YBa_2Cu_3O_{6.6}$, (5) Cu(2) in $YBa_2Cu_4O_8$, (6) Cu in $Bi_2Sr_2CaCu_2O_8$, (7) Cu in $Tl_2Ba_2CaCu_2O_8$, (8) Cu in $HgBa_2CuO_4$, and (9) Cu in $HgBa_2CaCu_2O_6$.

(ii) The limiting value of the isomer shift $[I.S.]$ at $T \rightarrow 0$ K, determined as $[I.S.]_0 = S_0 - D_0$ (where S_0 and D_0 are the spectrum centroid and Doppler shift at $T \rightarrow 0$ K).

We can see from Fig. 3 that $[I.S.]_0$ increases with the superconducting transition temperature of a compound. The value of $[I.S.]_0$ also depends on the site at which the Mössbauer probe is localized: the value is highest for Cu(2) sites, much lower for Cu(1) sites, and lowest for Y sites, if we compare the shifts for sites in the same lattice. For example, in the $YBa_2Cu_3O_{6.9}$ lattice, $[I.S.]_0 = 6.6, 2.9,$ and $1.9 \mu\text{m/s}$ for Cu(2), Cu(1), and Y sites, respectively.

The isomer shift of the Mössbauer spectra is directly related to the change in the electron density of ^{67}Zn nuclei; the values of $[I.S.]_0$ characterize the electron density caused by the Bose condensate under conditions where all the conduction electrons have formed Cooper pairs. Figure 3 shows the dependence of $\Delta|\Psi(0)|^2$ on T_c^{-1} ; the calibration of [12] was used in this case. The parameter $\Delta|\Psi(0)|^2 = |\Psi_c(0)|^2 - |\Psi_0(0)|^2$ increases with T_c , which indicates that the electron density at ^{67}Zn nuclei increases as a result of a superconducting transition. The quantities $|\Psi_0(0)|^2$ and $|\Psi_c(0)|^2$ are the electron densities at ^{67}Zn nuclei of the nonsuperconducting and superconducting phases, respectively.

The dependence of $\Delta|\Psi(0)|^2$ on T_c can be understood if it is taken into account that the standard correlation length ξ_0 (the Cooper pair “size” at $T \rightarrow 0$ K) in the Bardeen-Cooper-Schrieffer (BCS) theory is defined as

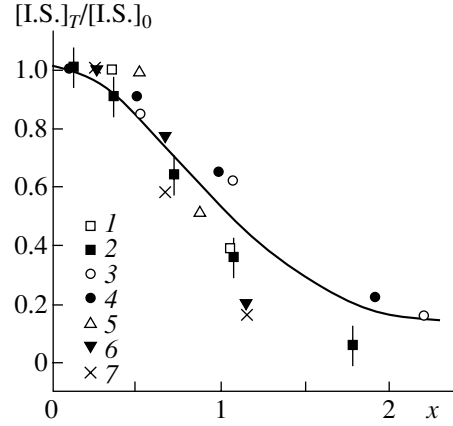


Fig. 4. Dependence of $[I.S.]_T/[I.S.]_0$ on the parameter $x = 1.76kT/\Delta$. The solid curve is the calculated dependence of the effective density of superfluid electrons on the parameter x . Symbols correspond to the data on (1) Cu in $Tl_2Ba_2CaCu_2O_8$, (2) Cu in $Bi_2Sr_2CaCu_2O_8$, (3) Cu in $HgBa_2CuO_4$, (4) Cu in $Hg_2Ba_2CaCu_2O_6$, (5) Cu in $Nd_{1.85}Ce_{0.15}CuO_4$, (6) Cu in $La_{1.85}Ce_{0.15}CuO_4$, and (7) Y in $La_{1.85}Ce_{0.15}CuO_4$.

$\xi_0 \propto T_c^{-1}$. Thus, Fig. 3 displays the dependence of $[I.S.]_0$ and $\Delta|\Psi(0)|^2$ on T_c^{-1} , i.e., on the standard correlation length ξ_0 . This dependence is exponential,

$$\Delta|\Psi(0)|^2(\text{au}) = 0.2(\text{au})\exp[(-31.4/T_c)].$$

It is evident that the greatest possible change in the electron density at ^{67}Zn nuclei during the superconducting transition is $\Delta|\Psi(0)|^2 = 0.2$ au, which corresponds to the smallest possible “size” ξ_0^{\min} of the Cooper pair. The existence of such a minimum size is probably caused by the physical impossibility of a Cooper pair existing with the distance between components shorter than a certain critical length. Assuming the dependence of $\Delta|\Psi(0)|^2$ on ξ_0 to be linear, we find that $\xi_0^{\min} \approx 2.5 \text{ \AA}$, which conforms with the conventional values $\xi_0^{\min} \approx 0.5\text{--}30 \text{ \AA}$ [13].

We note that, if the Cooper pair “size” is large (significantly larger than the atomic scale), the change in the electron density at ^{67}Zn nuclei is insignificant and it is hardly possible to reliably observe a change in the electron density for materials with $T_c < 10$ K using ^{67}Zn spectroscopy.

Within the BCS theory, the temperature dependence $\rho(T)$ of the effective density of superfluid electrons can be determined [14]; at the same time, it would be expected that $\rho(T) \propto [I.S.]_T/[I.S.]_0$. Therefore, the theoretical dependence of ρ on the parameter $x = 1.76(k_0T/\Delta)$ is shown in Figs. 4 and 5 (where k_0 is the Boltzmann constant and Δ is the energy gap in the spectrum of elementary excitations of the superconductor,

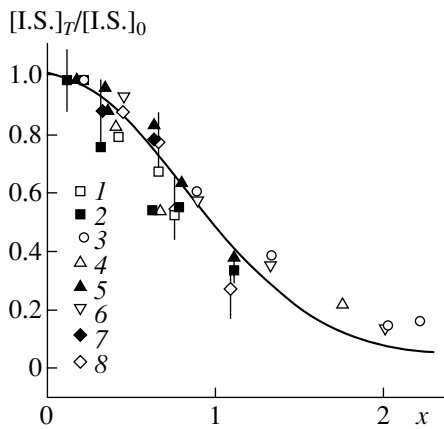


Fig. 5. Dependence of $[I.S.]_T/[I.S.]_0$ on the parameter $x = 1.76kT/\Delta$. The solid curve is the calculated dependence of the effective density of superfluid electrons on the parameter x . Symbols correspond to the data on (1) Cu(1) in $YBa_2Cu_3O_{6.6}$, (2) Cu(1) in $YBa_2Cu_3O_{6.9}$, (3) Cu(1) in $YBa_2Cu_4O_8$, (4) Cu(2) in $YBa_2Cu_3O_{6.6}$, (5) Cu(2) in $YBa_2Cu_3O_{6.9}$, (6) Cu(2) in $YBa_2Cu_4O_8$, (7) Y in $YBa_2Cu_3O_{6.9}$, and (8) Y in $YBa_2Cu_4O_8$.

taken from [14]) along with the data on the dependence of $[I.S.]_T/[I.S.]_0$ on the parameter x , which we measured for various compounds. Figures 4 and 5 show data on lattices containing a single-type sites and two structurally nonequivalent sites for copper atoms, respectively. We can see a satisfactory fit between the calculated and experimental temperature dependences of the effective density of superfluid electrons. Apparently, this agreement should be considered as evidence that the formation of Cooper pairs and their Bose condensation should necessarily be taken into account in any theory of high-temperature superconductivity. The special feature of the compounds presented in Fig. 5 lies in the fact that the values of $[I.S.]_0$ are found to be different for Cu(1), Cu(2), and Y sites. This is probably caused by the spatial nonuniformity of the electron density due to the Bose condensate of Cooper pairs. Nevertheless, satisfactory agreement between the calculated and experimental temperature dependences of the effective density of superfluid electrons has been found for Cu(1), Cu(2), and Y sites.

4. CONCLUSION

It was ascertained that the temperature dependence (at $T > T_c$) of the centroid S of the $^{67}Zn^{2+}$ -probe Mössbauer spectrum is controlled by a second-order Doppler shift for $YBa_2Cu_3O_{6.6}$, $YBa_2Cu_3O_{6.9}$, $YBa_2Cu_4O_8$, $Nd_{1.85}Ce_{0.15}CuO_4$, $La_{1.85}Ce_{0.15}CuO_4$, $HgBa_2CuO_4$, $HgBa_2CaCu_2O_6$, $Bi_2Sr_2CaCu_2O_8$, and $Tl_2Ba_2CaCu_2O_8$ compounds. In the region $T < T_c$, the quantity S depends on the formation of Cooper pairs and their Bose condensation. In the case of $YBa_2Cu_3O_{6.6}$, $YBa_2Cu_3O_{6.9}$,

and $YBa_2Cu_4O_8$ crystals containing two structurally nonequivalent sites for copper atoms, the change in the electron density, caused by the Bose condensation of Cooper pairs, was shown to be different for these sites, and for yttrium sites as well. The maximum change in the electron density was highest for Cu(2) sites, much lower for Cu(1) sites, and lowest for Y sites. The experimentally observed temperature dependence of the fraction of superconducting electrons satisfactorily agreed with a similar dependence following from the BCS theory for all of the Cu(1), Cu(2), and Y sites under study. A dependence between the change in the electron density at the metal crystal site and its superconducting transition temperature was found. In this case, the greatest possible change in the electron density exists at ^{67}Zn nuclei during the superconducting transition. It was assumed that this value corresponds to the smallest possible "size" of the Cooper pair, $\sim 2.5 \text{ \AA}$.

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REFERENCES

1. N. P. Seregin and P. P. Seregin, *Zh. Éksp. Teor. Fiz.* **118**, 1421 (2000) [*JETP* **91**, 1230 (2000)].
2. J. Capponi, C. Chaillout, A. Hewat, *et al.*, *Europhys. Lett.* **3**, 1301 (1987).
3. E. Kaldis, P. Fischer, A. W. Hewat, *et al.*, *Physica C (Amsterdam)* **159**, 668 (1989).
4. O. Chmaissem, Q. Huang, S. N. Putilin, *et al.*, *Physica C (Amsterdam)* **212**, 259 (1993).
5. E. V. Antipov, J. J. Capponi, C. Chaillout, *et al.*, *Physica C (Amsterdam)* **218**, 348 (1993).
6. J. M. Tarascon, W. R. McKinnon, P. Barboux, *et al.*, *Phys. Rev. B* **38**, 8885 (1988).
7. D. L. Nagy, in *Mössbauer Spectroscopy of Frozen Solutions*, Ed. by A. Vértes and D. L. Nagy (Akadémiai Kiado, Budapest, 1990; Mir, Moscow, 1998).
8. T. Sasaki, N. Kobayashi, O. Nakatsu, *et al.*, *Physica C (Amsterdam)* **153–155**, 1012 (1988).
9. H. M. Ledbetter, S. A. Kim, and R. B. Goldfarb, *Phys. Rev. B* **39**, 9689 (1989).
10. A. Junod, T. Craf, D. Sánchez, *et al.*, *Physica C (Amsterdam)* **165–166**, 1335 (1990).
11. S. J. Collocott, R. Driver, C. Audrikidis, and F. Pavese, *Physica C (Amsterdam)* **156**, 292 (1989).
12. A. Svane and E. Antoncik, *Phys. Rev. B* **34**, 1944 (1986).
13. *Physical Properties of High Temperature Superconductors*, Ed. by D. M. Ginsberg (World Sci., Singapore, 1989; Mir, Moscow, 1990).
14. J. R. Schrieffer, *Theory of Superconductivity* (Benjamin, New York, 1964; Nauka, Moscow, 1970).

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