MOSSBAUER STUDY OF ^{129}I IN HIGH T_c SUPERCONDUCTOR $YBa_2Cu_3O_6I_x$

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It has been shown recently /1—3/ that the treatment of tetragonal nonsuperconducting ceramics $YBa_2Cu_3O_6$ in halogen vapours recovers its superconducting properties. In the work /3/ a number of important questions were posed, the answers to which are important for understanding the specific features of the occurrence of high-temperature superconductivity (HTSC) in the halogen-doped system Y—Ba-Cu—O. In this work we have attempted to determine the charge states of iodine in this system using Mossbauer spectroscopy methods.

Samples of tetragonal nonsuperconducting ceramics $YBa_2Cu_3O_{6.1}$ were treated in ^{129}I vapours by the technique described in /3,4/. The chemical composition of a typical I-doped sample corresponded to the formula $YBa_2Cu_3O_{6.1}I_{0.96}$ wherein the content of ^{129}I was determined by a method of sulphide leaching described in /5/. The crystal structure of iodinated samples, as prompted by X-ray structural analyses data, corresponds to the orthorhombic phase with the parameters close to the earlier obtained ones /3,4/. No impurities of other phases were observed by X-ray methods. The measuring of the magnetic susceptibility $\varkappa_{ac}(T)$ of ^{129}I-doped samples demonstrates the occurrence of the superconducting transition with the onset at $T \approx 55$ K. This value also agrees well with the earlier obtained result.

The Mossbauer spectra of the transition $5/2^+ — 7/2^+$ in ^{129}I were measured in a transmission geometry. The source and the sample were at $T = 4.2$ K. The $5MgO \cdot {}^{129m}TeO_3$, prepared according to /6/, was used as a source. The obtained spectra are well described by the sum of subspectra, corresponding to two chemical forms of iodine. The spectral parameters of these forms are tabulated.

Fig. demonstrates the diagram of isomer shifts for some iodine compounds and for two forms, obtained by us (designated 1 and 2). A comparison of the obtained values of the isomer shifts for forms 1 and 2 with the known systematics for isomer shifts of ^{129}I compounds shows that the system studied involves the forms I^- and IO_6^{-5}, corresponding to formal valences of iodine —1 and +7. The ratio of quantity of iodide to that of IO_6^{-5} estimated from the spectral areas and corrected for the recoil-free fractions is approximately 24:1. So it is obvious that IO_6^{-5} — ion is present in very small quantities.

In order to estimate the iodide ion charge from the experimental value of the isomer shift and the isomer shift calibration data /7/, one should make an assumption on the degree of s—p hybridization of iodine valence electrons. Nevertheless, some limitations on the iodine charge can be obtained from the condition that a number of vacancies in the 5s — shell of iodine (h_s) is positive (which is just the requirement of Pauli's principle). Thus, putting $h_s \geqslant 0$ and substituting the iodide isomer shift value (0.19) for δ in the isomer shift calibration equation /7/

$$\delta = -(9 \pm 1)\, h_s + (1.5 \pm 0.1)\, h_p ,$$

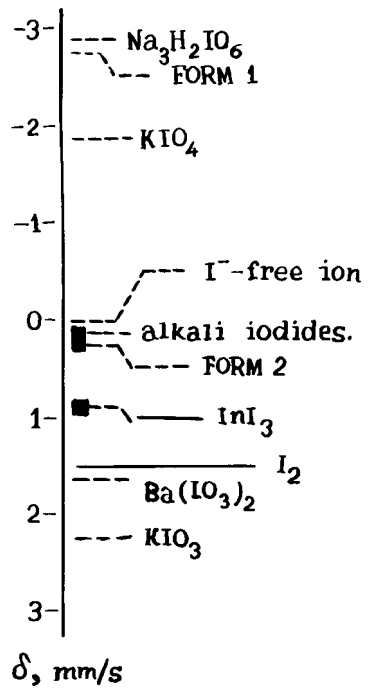

Fig. Diagram of isomer shifts for some iodine compounds and for two forms obtained by us in Y—Ba—Cu—O—I. Form 1 is 10^{-3} and Form 2 is iodide-ion

Table

	T=4.2K
T_{a1}, rel. un.	5.6%
T_{a2}, rel. un.	94.4%
δ_1, mm/s	—2.74 (5)
δ_2, mm/s	0.19 (1)
$\lvert e^2qQ_2\rvert$ (MHz)	52(3)
Γ, mm/s	1.07 (2)
M, %	0.3 (1)

Table of parameters of Mossbauer spectrum of the $YBa_2Cu_3O_{6.1}I_{0.96}$. T_a — effective thickness, δ — isomer shift, $e^2q^{129}Q$ — quadrupole coupling constant, Γ — line width, M — misfit criterion '1' and '2' refer to corresponding forms (fig.)

we obtained the limitation on $h_p \geqslant 0.13$. This means that the iodide ion charge Q_I is in the range $0 \geqslant Q_I \geqslant -0.87$.

Note that the charge value is very sensitive to the dergee of the s—p hybridization. For example, $h_s=0.05$ for the given value $\delta=0.19$ requires $h_p=0.45$ and then $Q_I \cong -0.5$. As the iodide-ion charge changes from —1 to 0, its dimension has to decrease from the ionic radius (2.16 Å) to the covalent radius (1.33 Å) /8/.

REFERENCES

1. *Ossipyan Yu. A., Zharikov O. V., Sidorov N. S. et al.* Pis'ma JETP. 1988. 48. 225.
2. *Klimenko A. G., Kuznetsov V. I. et al.* Preprint 88-24. 1988. IIC SO AS USSR.
3. *Ossipyan Yu. A., Zharikov O. V. et. al.* Pis'ma JETP. 1989. 49. 61.
4. *Ossipyan Yu. A., Zharikov O. V., Novikov G. V., Sidorov N. S., Kulakov V. I., Sypavina L. V., Nikolaev R. K., Gromov A. M.* Physica C. 159 1989. 137—140.
5. *Grushko Yu. S.* Avtorskoe Svidetel'stvo N 417007. 26.10.1973.
6. *Alexandrov A. J., Grushko J. S., Makarov E. F., Mishin K. Y., Baltrunas D. A. J.* U. S. Patent 4.004.970, Jan.25, 1977.
7. *de Waard H.* 1973. Mossbauer Effect Data Index, ed. *Stevens J. G., Stevens V. E.* (N.—Y.:Plenum). 1975.
8. *Pauling L., Pauling P.* Chemistry. Moscow. 1978. . 153—154.