Spatial distribution of Bose condensate in high-temperature superconductors, determined by emission Mössbauer spectroscopy

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Abstract

It has been shown that temperature dependences of the gravity centres of ^{67}Cu(^{67}Zn) and ^{67}Ga(^{67}Zn) emission Mössbauer spectra of $Nd_{1.85}Ce_{0.15}CuO_4$, $La_{1.85}Sr_{0.15}CuO_4$ and $Tl_2Ba_2Ca_2CuO_8$ superconductors are described by the second-order Doppler shift in the temperature range $T > T_c$, and Bose condensation of Cooper pairs should be taken into account at $T < T_c$ (T_c is the superconducting transition temperature). The spatial nonuniformity of the electron density created by the Bose condensate has been observed in $La_{1.85}Sr_{0.15}CuO_4$.

1. Introduction

The superconductivity phenomenon appears owing to the creation of Cooper pairs and their Bose condensate, described by a single coherent wavefunction [1]. This means that the distribution of the electron density within the superconductor lattices must be affected by different processes at temperatures above and below the superconducting transition temperature T_c.

It is possible, in principle, to reveal Bose condensation by measuring how the gravity centre S of Mössbauer spectra of superconductors depends on temperature. This possibility arises from the fact that the isomer shift δ of the spectra depends on the electron density at the Mössbauer nuclei. The temperature dependence of S is determined at constant pressure P by three terms [2]:

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial \delta}{\partial \ln V}\right)_T \left(\frac{\partial \ln V}{\partial T}\right)_P + \left(\frac{\partial D}{\partial T}\right)_P + \left(\frac{\partial \delta}{\partial T}\right)_V. \tag{1}$$

The first term in equation (1) represents the dependence of the isomer shift δ on volume V. If no structural phase transitions take place in a compound within the investigated temperature range, this term is negligibly small.

The second term describes the second-order Doppler shift D and can be represented in the Debye approximation as [2]:

$$\left(\frac{\partial D}{\partial T}\right)_P = -\frac{3k_B E_o}{2Mc^2} F(T/\theta), \tag{2}$$

where k_B is the Boltzmann constant, E_o the isomer transition energy, M the probe nucleus mass, c the speed of light in vacuum, θ the Debye temperature, and $F(T/\theta)$ the Debye function. The Debye model is known to give a full description of vibration properties for primitive lattices only. However, equation (2) is also commonly used to describe experimental temperature dependences $S(T)$ for compounds with complex crystal structure [3–7]. This seems to be accounted for by the fact that the temperature dependence of the Doppler shift is mainly controlled by the long-wavelength region of the vibration spectra, described satisfactorily by the Debye approximation.

Finally, the third term in equation (1) represents the temperature dependence of the isomer shift δ at constant volume. This term should be taken into account because the electron density at Mössbauer nuclei is expected to change upon transition to the superconducting state. However, no reliable theoretical estimations of the extent of this change are currently available and only experimental investigations can confirm the possibility of observing Cooper pairs and their Bose condensation by Mössbauer spectroscopy.

In particular, the authors of [3] made an attempt to observe Cooper pairs in the temperature dependence of the gravity centre of a ^{119}Sn Mössbauer spectrum for the well-known Nb_3Sn superconductor. However, they found that the second-order Doppler shift satisfactorily describes the measured $S(T)$ data and no specific features that could be assigned to isomer shift changes are observed near T_c.

Several attempts to detect Bose condensation have been made after the discovery of the high-temperature superconductivity in complex copper oxides. Compounds including intrinsic Mössbauer atoms are of specific interest in this connection. Such investigations are known only for the $EuBa_2Cu_3O_{7-x}$ compound ($T_c \sim 80$ K) with the ^{151}Eu isotope [4, 5]. The temperature dependences of the gravity centres of ^{151}Eu Mössbauer spectra were found to be described by the second-order Doppler shift in the Debye approximation and no features were established near T_c. Similar results have been obtained for $YBa_2Cu_3O_{7-x}$ by means of the ^{57}Fe impurity Mössbauer spectroscopy [6].

Thus, observation of the effect of the superconducting transition on the electron density at nuclei is still an unresolved problem of both the Mössbauer spectroscopy and superconductivity physics. This fact can be accounted for by the small values of the $\Delta\delta/G$ parameter ($\Delta\delta$ is the maximum achievable difference between the isomer shifts in the ordinary and superconducting phases, G is the full width at half-maximum of experimental spectra), which do not exceed 5 for ^{57}Fe, ^{119}Sn and ^{151}Eu. More favourable conditions for finding the effect of Cooper pairs on the electron density distribution must be achieved when investigating high-temperature superconductors (having the minimum scale of Cooper correlation length) with a probe with $\Delta\delta/G \gg 10$. In addition, the objects of study should be chosen so as to provide introduction of the Mössbauer probe at a certain lattice site. Both of the above requirements are satisfied for ^{67}Cu(^{67}Zn) emission Mössbauer spectroscopy with ^{67}Zn probe in copper metal-oxide lattices. The $\Delta\delta/G$ value is estimated to be 50–200 for ^{67}Zn, and parent ^{67}Cu atoms occupy copper sites in synthesis, so that daughter ^{67}Zn atoms are situated at the same lattice sites [8–10]. In addition, another parent nucleus ^{67}Ga used in ^{67}Ga(^{67}Zn) emission Mössbauer

spectroscopy allows one to introduce the ^{67}Zn probe at rare-earth sites [11] of high-temperature superconductors containing rare-earth metals, thus making it possible to study the spatial nonuniformity of the electron density created in Bose condensation of Cooper pairs. Finally, it should be noted that the ^{67}Zn probe is a part of a two-electron Zn centre with negative correlation energy [12]. Its charge state can only be changed by simultaneous transfer of two electrons. The electron pair localized at the centre has zero total momentum, orbital momentum and spin. On the other hand, electrons with opposite momentums are paired at $T < T_c$ according to the BCS model, so that the total momentum, orbital momentum, and spin of a Cooper pair are also zero. Such a combination of properties may be favourable for observing the Bose condensation with the use of the ^{67}Zn probe.

The present paper reports the results of ^{67}Zn Mössbauer investigations of $Nd_{1.85}Ce_{0.15}CuO_4$, $La_{1.85}Sr_{0.15}CuO_4$ and $Tl_2Ba_2Ca_2CuO_8$ superconductors.

2. Experimental results and discussion

The Mössbauer sources $Nd_{1.85}Ce_{0.15}CuO_4$, $La_{1.85}Sr_{0.15}CuO_4$ and $Tl_2Ba_2Ca_2CuO_8$ were prepared by diffusing radioactive carrier-free ^{67}Cu into polycrystalline samples in an oxygen flow at 450 °C for 2 h. $La_{1.85}Sr_{0.15}CuO_4$ was also doped by diffusion of radioactive carrier-free ^{67}Ga under similar conditions. Two sets of starting materials were used. The first consisted of $Nd_{1.85}Ce_{0.15}CuO_4$, $La_{1.85}Sr_{0.15}CuO_4$ and $Tl_2Ba_2Ca_2CuO_8$ superconducting samples with T_c of 22, 37 and 60 K, respectively. No noticeable changes in T_c were observed for these samples after the diffusion annealing. The second (test) set consisted of samples of the same nominal composition, subjected to thermal treatment in a vacuum at 1300 °C for 2 h. No superconductivity was observed for this set, at least down to 4.2 K. Spectra of the test set were used for comparison with the spectra of corresponding samples of the first set. Such a comparison must make clearer the similarity of the temperature dependences of the spectra or their difference.

^{67}Zn Mössbauer spectra were recorded in the conventional transmission geometry with a modified commercial MS–2201 spectrometer. The electrodynamic drive of the spectrometer was replaced with a piezoelectric device based on the PZT ceramics. A piezoceramic cylinder was set up within a cylindrical perspex unit and put in motion an aluminium container with ^{67}ZnS absorber (surface density of 1 g cm^{-2} in terms of ^{67}Zn). The sources were fixed at the opposite end of the perspex unit. The motion was produced by an integrated and amplified low-frequency drive signal from the base spectrometer. The drive system included no feedback. The velocity range ± 150 μm s^{-1} was scanned. The velocity scale was calibrated by means of the quadrupole hyperfine pattern of ^{67}ZnO. Gamma-radiation was detected with a Ge(Li) device sensitized in the 100 keV region.

The sources and the absorber were situated in two separate chambers of the perspex unit. They were both cooled by helium gas flow and their temperatures were measured by semiconductor sensors. The absorber was kept at 10 ± 2 K, whereas the source temperature could be raised up to 80 K and controlled with the same accuracy.

The Mössbauer spectra were well-resolved quadrupole triplets for all the ceramics within the above temperature range. Their isomer shifts corresponded to ^{67}Zn^{2+} ions. Typical spectra of the $La_{1.85}Sr_{0.15}CuO_4$ ceramics are shown in figure 1. The proposed interpretation of the ^{67}Cu(^{67}Zn) spectra assumes that parent ^{67}Cu atoms occupy copper sites upon diffusion doping, which is confirmed by [8–10], and, therefore, the ^{67}Zn^{2+} probe produced in ^{67}Cu decay occupies the copper site, too. For the $La_{1.85}Sr_{0.15}CuO_4$:^{67}Ga spectra, it was assumed that the diffusion doping causes parent ^{67}Ga atoms to occupy lanthanum sites, and, therefore, the ^{67}Zn^{2+} probe formed in ^{67}Ga decay also occupies the lanthanum site. This assumption
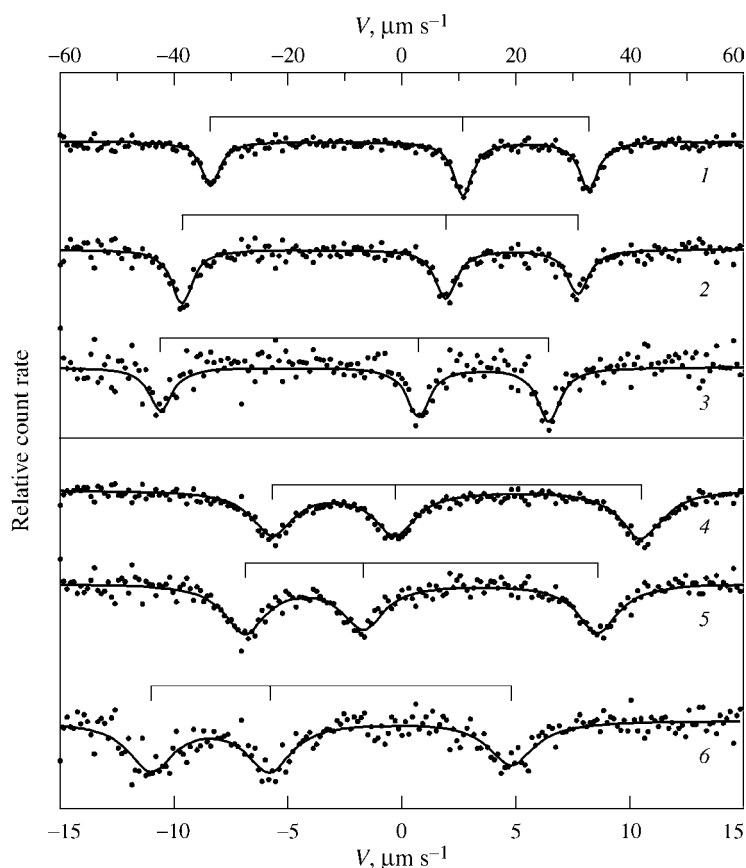
Figure 1. Mössbauer spectra of $La_{1.85}Sr_{0.15}{}^{67}CuO_4$ (curves 1–3) and $La_{1.85}Sr_{0.15}CuO_4:{}^{67}Ga$ (curves 4–6) samples at varied source temperature (absorber temperature 10 ± 2 K): 10 K (curve 1), 11 K (curve 4), 37 K (curves 2 and 5), 70 K (curve 3) and 75 K (curve 6). The components of the quadrupole triplets corresponding to ${}^{67}Zn^{2+}$ centres at copper and lanthanum sites are shown.

can be verified by the C–V_{zz} diagram [11] demonstrating a straight-line correlation between the ${}^{67}Zn$ quadrupole interaction constants C, obtained from emission Mössbauer spectra of $RBa_2Cu_3O_7:{}^{67}Ga$ compounds, and the principal components V_{zz} of the lattice electric field gradient tensors, calculated for rare-earth metal R sites (figure 2). It is seen that the point corresponding to $La_{1.85}Sr_{0.15}CuO_4:{}^{67}Ga$ lies on the straight line, too.

The quadrupole interaction constants C were found to be virtually temperature-independent for all the ceramics. This is an expected result, because the electric field gradient at the ${}^{67}Zn^{2+}$ probe is produced by the lattice ions only [8–11], and variations of the lattice constants in the temperature range 4.2–80 K are negligibly small [13, 14].

The temperature dependences of the gravity centre position S are shown in figures 3–5. They differ substantially between the spectra of superconducting and test samples. The plotted S values are given with respect to their values at T_c. As seen from figures 3–5 the $S(T)$ dependences for the test (nonsuperconducting) samples are described in the temperature range from 10 to 78 K by equation (2) with Debye temperatures of 360 ± 20, 400 ± 20 and 260 ± 20 K for $Nd_{1.85}Ce_{0.15}CuO_4$, $La_{1.85}Sr_{0.15}CuO_4$ and $Tl_2Ba_2Ca_2CuO_8$, respectively. According to heat capacity measurements, the corresponding Debye temperatures are 300 K [15], 420 K [16] and 270 K [16]. In other words, the isomer variations caused by the first and third terms in
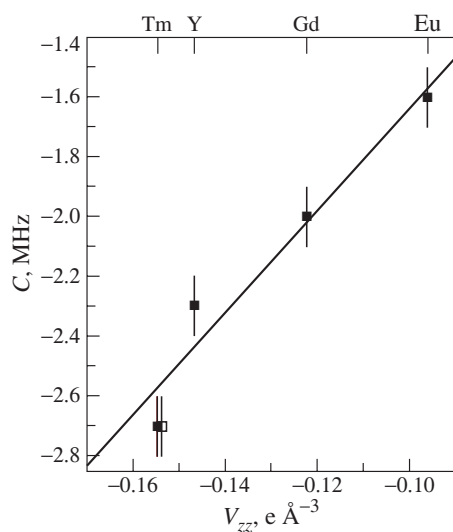
Figure 2. Quadrupole interaction constant C for rare-earth metal sites (experimental data obtained by emission Mössbauer spectroscopy) versus the principal components of the tensor of the crystal gradient of the electric field V_{zz} at the same sites (the computational results were obtained in the point-charge approximation) for $RBa_2Cu_3O_7$, $R = Y$, Eu, Gd, Tm (small filled squares). The large open square represents our data for lanthanum sites in $La_{1.85}Sr_{0.15}CuO_4$.
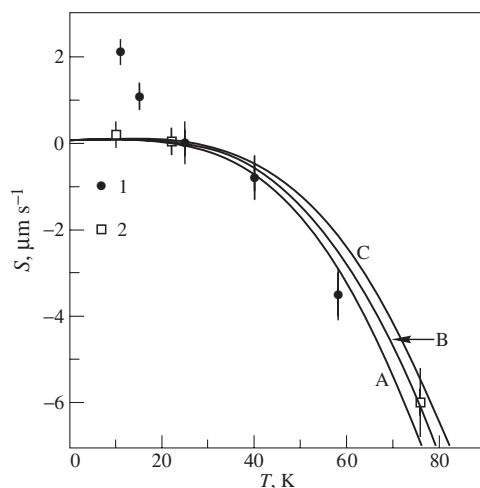

Figure 3. Temperature dependences of the gravity centre S of the ^{67}Zn Mössbauer spectra, measured relative to its value at 22 K, for superconducting (points 1) and nonsuperconducting (points 2) $Nd_{1.85}Ce_{0.15}{}^{67}CuO_4$. The theoretical temperature dependences of S are presented for the second-order Doppler shift with $\theta = 340$ K (curve A), 360 (curve B) and 380 (curve C).

equation (1) are negligibly small for the nonsuperconducting samples. This behaviour of $S(T)$ seems to be expected because no structural phase transitions are known for the investigated substances in the temperature range from 10 to 80 K [17].

Figures 3–5 also show the temperature dependences of S for superconducting samples $Nd_{1.85}Ce_{0.15}CuO_4$, $Tl_2Ba_2CaCu_2O_8$ and $La_{1.85}Sr_{0.15}CuO_4$. At $T > T_c$, the experimental data are described by equation (2), as in the case of nonsuperconducting samples, whereas significant
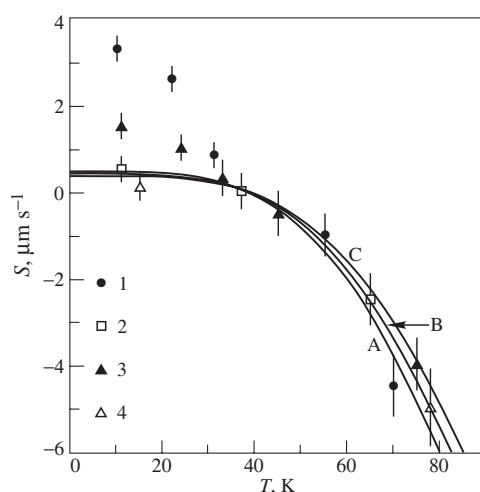
Figure 4. Temperature dependences of the gravity centre S of the ^{67}Zn Mössbauer spectra, measured relative to its value at 37 K, for $La_{1.85}Sr_{0.15}{}^{67}CuO_4$ (points 1, 2) and $La_{1.85}Sr_{0.15}CuO_4:{}^{67}Ga$ (points 3, 4). Superconducting samples (points 1, 3) and nonsuperconducting ones (points 2, 4). The theoretical temperature dependences of S are presented for the second-order Doppler shift with $\theta = 380$ K (curve A), 400 K (curve B) and 420 K (curve C).
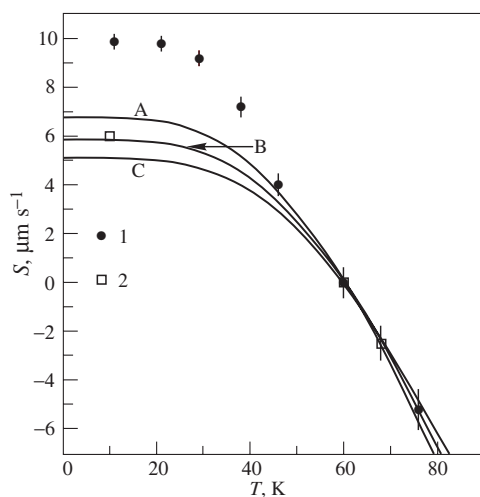

Figure 5. Temperature dependences of the gravity centre S of the ^{67}Zn Mössbauer spectra, measured relative to its value at 60 K, for superconducting (points 1) and nonsuperconducting $Tl_2Ba_2Ca^{67}Cu_2O_8$ (points 2). The theoretical temperature dependences of S are presented for the second-order Doppler shift with $\theta = 240$ K (curve A), 260 K (curve B) and 280 K (curve C).

deviations from equation (2) are seen at $T < T_c$. Calculations [18] showed that the first term in equation (1) cannot exceed 0.03 $\mu m\,s^{-1}$ for ^{67}Zn, and, therefore, the third term in equation (1) should be taken into account.

This term appears owing to a change in the electron density at the ^{67}Zn nuclei. The δ value at temperature T can be found as the difference $\delta_T = S_T - D_T$ (here S_T and D_T are the gravity centre of the spectrum and the second-order Doppler shift, respectively). The
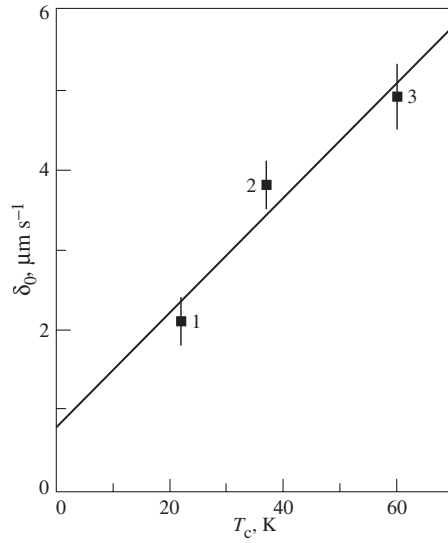
Figure 6. δ_0 versus T_c. The symbols represent the $Nd_{1.85}Ce_{0.15}{}^{67}CuO_4$ (point 1), $La_{1.85}Sr_{0.15}{}^{67}CuO_4$ (point 2) and $Tl_2Ba_2Ca^{67}Cu_2O_8$ (point 3) compounds.

increase in δ_T with decreasing temperature shows that the electron density at the ^{67}Zn nuclei grows in the $T < T_c$ range owing to the creation of Cooper pairs and their Bose condensation. The limiting value of δ at $T \rightarrow 0$, δ_0, must depend on the Cooper pair size. In its turn, this size is known to depend on T_c [19]. This means that a correlation is expected between the δ_0 and T_c values. This correlation is shown in figure 6: with increasing T_c (i.e. decreasing Cooper correlation radius), the δ_0 value also grows as a result of a rise in the electron density at the $^{67}Zn^{2+}$ nuclei. It is important that $\delta_0 = 1.5 \pm 0.3$ μm s^{-1} for $^{67}Zn^{2+}$ centres at the lanthanum sites of $La_{1.85}Sr_{0.15}CuO_4$ is essentially different from zero and much smaller than $\delta_0 = 3.8 \pm 0.3$ μm s^{-1} for $^{67}Zn^{2+}$ centres at the copper sites of the same lattice (see figure 4). These relations show that, firstly, the isomer shift variations are determined not only by direct contribution of conductivity electrons (otherwise, δ_0 would be zero for the lanthanum sites because the conductivity electrons are placed in the Cu–O plane rather than at the La sites), and, secondly, the spatial distribution of the electron density created by the Bose condensate of the Cooper pairs is nonuniform.

Thus, it has been established that the temperature dependence of S for the $Nd_{1.85}Ce_{0.15}CuO_4$, $La_{1.85}Sr_{0.15}CuO_4$ and $Tl_2Ba_2Ca_2CuO_8$ superconductors is determined by the second-order Doppler shift in the $T > T_c$ range, whereas the S value is also affected by the creation of Cooper pairs and their Bose condensation at $T < T_c$. The Bose condensate fraction grows with decreasing temperature, and, therefore, its effect on the S value becomes more pronounced.

Generally, the temperature dependence of the effective density $\rho(T)$ of superfluid electrons can be written [1] as

$$\frac{\rho(T)}{\rho(0)} = 1 - \frac{2\beta E_F}{K_F^5} \int_0^\infty k^4 \frac{\exp(\beta E_k)}{[\exp(\beta E_k) + 1]^2} \, dk,$$

where $E_F = k_F^2/2m$ is the Fermi energy, m the electron mass, k the wavenumber, k_F the wavenumber at the Fermi surface, E_k the energy of the state with wavenumber k, $\beta = 1/k_B T$, and the equation $\rho(0) = k_F^3/3\pi^2$ means that all valence electrons are superfluid at $T = 0$.
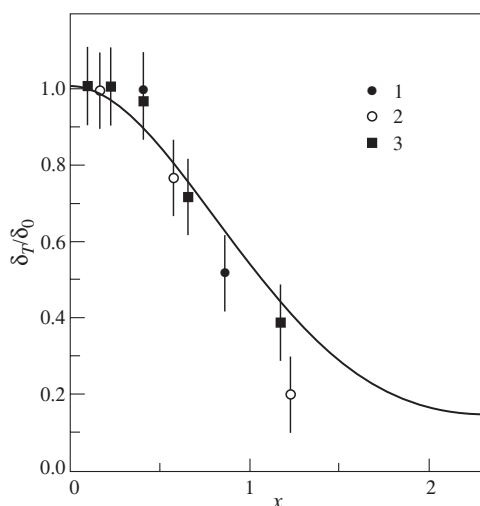
Figure 7. δ_T/δ_0 versus the parameter $x = 1.76(k_B T/\Delta)$. The solid curve shows the theoretical dependence of the effective density of superfluid electrons on the parameter x. The symbols represent $Nd_{1.85}Ce_{0.15}{}^{67}CuO_4$ (points 1), $La_{1.85}Sr_{0.15}{}^{67}CuO_4$ (points 2), and $TI_2Ba_2Ca{}^{67}Cu_2O_8$ (points 3).

On the other hand, the effect of Bose condensation on the isomer shift is expected to be proportional to the number of electrons being transferred to the lowest state, i.e. $\delta_T \sim \rho(T)$. To bring these values to a common scale, they should be divided by δ_0 and $\rho(0)$, respectively. For this reason, figure 7 shows the theoretical dependence of ρ on the parameter $x = 1.76(k_B T/\Delta)$ [1] ($\Delta = 3.06 k_B \sqrt{T_c(T_c - T)}$ is the energy gap in the elementary excitation spectrum of the superconductor) together with our δ_T/δ_0 data obtained by the ${}^{67}Cu$ (${}^{67}Zn$) emission spectroscopy and plotted against the same parameter x. A satisfactory agreement between the calculated and experimental values is observed. In other words, ${}^{67}Zn$ Mössbauer spectroscopy can be proposed as an effective method for studying Cooper pairs and their Bose condensation in high-temperature superconductors.

Unfortunately, no clear models are currently available for describing the observed rise in the electron density at the nuclei of the ${}^{67}Zn$ impurity centres below T_c. It is possible, for example, to regard the above rise as resulting from a change in the charge state of the Zn impurity. However, this interpretation must resolve two problems. Firstly, the measured δ_0 values of about 2–5 $\mu m\ s^{-1}$ are considerably lower than the value of 165 $\mu m\ s^{-1}$ expected for the $Zn^{2+} \longrightarrow Zn^0$ transition [18]. This discrepancy can be accounted for if we assume that the effective localization radius for an electron pair at the impurity centre is much larger than the Zn^{2+} ionic radius. For instance, one could take the Cooper correlation length ($\sim 10^{-7}$ cm for HTSC's) as the localization radius. Secondly, the Zn charge state is determined by the position of the Zn impurity level relative to the Fermi level. Therefore, the Zn level must lie significantly higher than the Fermi level at $T > T_c$, so that the impurity charge state is independent of temperature. In contrast, the observed temperature dependence of S at $T < T_c$ means that the Zn level is pinned to the Fermi level to within $k_B T$.

Another possible explanation assumes that the observed increase in the electron density at Zn nuclei is caused by spatial redistribution of electrons as a result of the Bose condensation. The main difficulty of this interpretation is that it is necessary to prove the possibility of observing, in principle, the above redistribution by means of an impurity probe.

The Zn probe forms a two-electron centre with negative correlation energy [12]. An s-electron pair localized at this centre has zero values of all total angular, orbital and spin momentums. On the other hand, the BCS model requires pairing of electrons with opposite momentums so that the total linear momentum, orbital momentum and spin of a Cooper pair are also zero. A combination of these properties could provide conditions for the Bose condensation to affect the electron density at the ^{67}Zn probe. However, one should take into account that the BCS model requires s-pairing, whereas the paired electrons in HTSC's are currently believed to have d-symmetry [20]. For this reason, the agreement between the measured and calculated dependences of the electron densities at $T < T_c$, established here (figure 6), seems to require additional consideration.

3. Conclusion

Emission Mössbauer spectroscopy with ^{67}Cu(^{67}Zn) and ^{67}Ga(^{67}Zn) isotopes was applied to reveal a redistribution of electron density upon transition to the superconducting state in $Nd_{1.85}Ce_{0.15}CuO_4$, $La_{1.85}Sr_{0.15}CuO_4$ and $Tl_2Ba_2Ca_2CuO_8$ compounds. ^{67}Zn emission Mössbauer spectroscopy is proposed as a method for investigating the Bose condensation of Cooper pairs. A spatial nonuniformity of the electron density, produced by the Bose-condensate of Cooper pairs, was found.

Acknowledgments

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