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NMR and Spin-Lattice Relaxation Rate of ^{89}Y, ^{63}Cu in Radiation Disordered $YBa_2Cu_3O_{6.9}$

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Abstract. NMR line shifts and spin-lattice relaxation rates of ^{89}Y and ^{63}Cu in $YBa_2Cu_3O_{6.9}$ were measured in disordered samples irradiated by fast neutrons with a fluence of: $\varphi = 5 \cdot 10^{18}$ cm^{-2} ($T_c^{ons} = 70$ K), $\varphi = 1.2 \cdot 10^{19}$ cm^{-2} ($T_c^{ons} = 20$ K), in order to investigate the evolution of spin susceptibility χ_S under irradiation. According to the data obtained, χ_S decreases markedly as structural disorder accumulates in the samples. The variation of χ_S is related closely to that observed in oxygen-depleted $YBa_2Cu_3O_{7-\delta}$ compounds with nearly the same T_c value. The data for yttrium display some features that are absent in oxygen-depleted samples. The different temperature dependence of the ^{89}Y and ^{63}Cu Knight shifts and the increase of the ^{89}Y spin-lattice relaxation rate in irradiated samples are discussed in terms of the electron localization effects arising in the CuO_2 planes due to the radiation-induced structural disorder.

1. Introduction

In the past years many efforts have been undertaken to ascertain the features peculiar to the electron spectrum of high-T_c superconducting cuprates [1]. Special attention was paid to the influence of hole doping of the oxygen states near the Fermi energy on the strong antiferromagnetic spin fluctuations at $Q = (\pi/a, \pi/a)$ in the perovskite CuO_2 layer. NMR studies of $YBa_2Cu_3O_{7-\delta}$ [2–5] gave evidence for the presence of a strong correlation between the copper d-spin and the oxygen p-hole systems. The values of the magnetic hyperfine interaction constant were found to be independent of δ. Within the framework of the phenomenological "antiferromagnetic Fermi-liquid" model, D.Pines, H.Monien and J.Millis proposed a quantitative description of the temperature dependences of the NMR line shift and spin-lattice relaxation data for different atoms (^{17}O, ^{89}Y, ^{63}Cu) by using a single spin-spin correlation function and a proper dynamic spin susceptibility $\chi_S(q,\omega)$. In oxygen depleted $YBa_2Cu_3O_{7-\delta}$, the uniform part of the spin susceptibility $\chi_S(0,0)$ decreases with increasing magnetic correlation length ξ_m, which describes the spatial correlation of AF spin fluctuations in the CuO_2 plane.

As is known, the phenomenon of high-T_c superconductivity in oxides appears near the metal-insulator transition. In part, that explains the extremely high sensitivity of superconducting properties on structural and chemical disorder in oxides. Studying the influence of structural disorder on the spin susceptibility is a question of great interest. Radiation disordering by fast neutrons at low temperature is probably the purest method to study the influence of the induced structural disorder on the physical properties of high-T_c oxides. In this case the chemical composition does not change: $\Delta\delta < 0.1$. Increased disorder leads to a sharp drop of T_c values and to a number of changes in transport properties, changes which point to the appearance of localization effects in the electron spectrum near the Fermi energy. The data [8,9] provide evidence for a continuous metal-insulator transition at very light disorder, for the coexistence of hopping conductivity and superconductivity at intermediate disorder and for an anomalous (exponential) growth of resistivity with increasing defect concentration. Magnetic susceptibility measurements and an analysis of ^{63}Cu NQR line intensities for Cu1 and Cu2 positions in irradiated $YBa_2Cu_3O_{6.9}$ [8,10] show that local magnetic moments appear in the CuO_2 plane. The concentration of moments is proportional to the neutron flux φ. Taking into account the proper Curie-like contribution of the defects to the magnetic susceptibility an increase of the temperature-independent part χ_O for irradiated samples was observed.

The purpose of this paper is to study the variation of the spin contribution to magnetic susceptibility in radiation disordered $YBa_2Cu_3O_{6.9}$ by measuring the NMR line shifts and spin-lattice relaxation rates of ^{89}Y and ^{63}Cu nuclei. As accepted [2–6] the Knight shift of ^{63}Cu and ^{89}Y and the spin-lattice relaxation rate of ^{89}Y are proportional to the static part of magnetic susceptibility. In turn, the spin-lattice relaxation rate of copper, $T_1^{-1}(^{63}\mathrm{Cu}) \equiv {}^{63}R$, is mainly determined by the low-frequency spin dynamics near $q = Q_{AF}$. When electron localization effects become sizeable, one may expect an increase in the time needed for an electron travelling at the Fermi velocity in order to traverse one nearest neighbor distance. That will enhance the spectral intensity of the hyperfine magnetic field fluctuations near the Larmor frequency and give rise to $T_1^{-1}(^{89}\mathrm{Y})$ in comparison with the relation predicted by Korringa.

2. Experimental Technique and Samples

The measurements were performed on ceramic samples of $YBa_2Cu_3O_{6.9}$, which were uniaxially oriented in the magnetic field $B_0 = 8.0$ T for ^{63}Cu NMR experiments. The value of the critical temperature, $T_c^{ons} = 94.5$ K, and the superconducting transition width, $\Delta T_c = 3$ K, were determined from AC susceptibility measurements. Irradiation by fast neutrons ($E > 1$ MeV) of original $YBa_2Cu_3O_{6.9}$ was carried out at temperature of liquid nitrogen. Results of X-Ray and neutron-diffraction structural investigations of irradiated samples are quoted in [11]. In $YBa_2Cu_3O_{6.9}$, this radiation-induced disordering is mainly due to oxygen redistribution over the crystallographic O4 and O5 sites in the Cu1-O planes. The total oxygen content of the samples remains practically unchanged: $\Delta\delta < 0.1$. Superconductivity disappears for $\varphi > 1.5 \cdot 10^{18}$ cm^{-2} in the orhorhombic phase of $YBa_2Cu_3O_{6.9}$.

NMR experiments were carried out over the temperature range 4.2 ÷ 300 K in samples of $YBa_2Cu_3O_{6.9}$ irradiated by fluences $\varphi = 0$ with $T_c^{ons} = 94.5$ K; $\varphi = 5 \cdot 10^{18}$ cm^{-2}, $T_c^{ons} = 70$ K, $\Delta T_c = 8$ K and $\varphi = 1.2 \cdot 10^{19}$ cm^{-2}, $T_c^{ons} = 20$ K, $\Delta T_c = 10$ K. Measurements of the NMR and NQR spectra of copper were performed using a Bruker SXP 4-100 NMR pulse spectrometer by means of the h.f. phase-sensitive detection of the spin-echo signal amplitude with a discrete scan of the resonance frequency. The delay time between the pulses forming an echo did not exceed 30 μs in our measurements. The NMR spectra were obtained in a magnetic field $B_0 = \nu_0 / \gamma = 8.0186$ T for parallel and perpendicular orientations of the c axis of the crystallites with respect to the magnetic field direction.

In order to determine the NMR line shift components for parallel $^{63}K_\parallel$ and perpendicular $^{63}K_\perp$ orientations, we measured the positions of the line maximum $\nu_{\parallel(\perp)}$ for the central transition $-1/2 \longleftrightarrow 1/2$ and took into account the results of ^{63}Cu NQR line position ν_Q measurements [10]. We have analyzed the data by assuming an axial symmetry of the electric field gradient and the NMR shift tensors for the Cu2 positions, restricting ourselves to the second order of the quadrupole coupling corrections to the central line of the ^{63}Cu NMR spectrum:

$$\nu_\parallel = \nu_0(1 + K_\parallel), \tag{1}$$

$$\nu_\perp = \nu_0(1 + K_\perp) + \frac{3}{16}\frac{\nu_Q^2}{\nu_0}. \tag{2}$$

In the superconducting state, additional terms arise in Eqs.(1) and (2) because of the incomplete Meissner effect. For $B_0 \cong 8$ T the value of this negative correction did not exceed the error in determining $^{63}K_\perp$(Cu2) in agreement with [6].

The ^{89}Y NMR spectra were obtained by Fourier-transform of the free induction decay signal following a single pulse.

Spin-lattice relaxation measurements were performed at the NQR frequency $\nu = 31$ MHz for ^{63}Cu and at $\nu_{NMR} = 16.7$ MHz for ^{89}Y. The ^{89}Y spin-lattice relaxation rate $T_1^{-1}(^{89}Y)$ was determined from a recovery of the spin echo amplitude $A(t)$ by varying the repetition time between the echo pulse sequences. For measuring the ^{63}Cu spin-lattice relaxation rate, we used a saturation recovery method. For all samples, the recovery curve $A(t)$ could be satisfactorily described by a one-exponential dependence in the temperature region of the normal state.

3. Experimental Results and Discussion

3.1. NMR Line Shift of Copper

The temperature dependence of the ^{63}Cu NMR line shift for copper in the CuO_2 plane are shown in Fig.1 ($\vec{H}_0 \parallel \vec{c}$) and Fig.2 ($\vec{H}_0 \perp \vec{c}$). For the non-irradiated $YBa_2Cu_3O_{6.9}$ sample, our results are in good agreement with the ^{63}Cu NMR shift data reported in [4,12,13] and reflect the temperature-independent behavior of the copper NMR shift above T_c . The decrease of $^{63}K_\perp$ in the superconducting state, $^{63}K_\perp(100\ \mathrm{K}) - K_\perp(15\ \mathrm{K}) = 0.26$ %, is also closely related to the results reported in [4] for $YBa_2Cu_3O_7$ compounds. This difference gives the value of the spin contribution $^{63}K_S$ to the total NMR magnetic shift. By taking into account the values of the magnetic hyperfine constants, $A_\perp = 32$ kOe/μ_B and $B = 40.3$ kOe/μ_B [6], we can estimate the spin contribution to the magnetic susceptibility of a non-irradiated $YBa_2Cu_3O_{6.9}$: $\chi_S/2\mu_B = 2.3(\mathrm{eV\ at\ Cu})^{-1}$. These hyperfine constants describe the copper on-site interaction $A_{\alpha\alpha}$ and the Cu—O—Cu supertrans-

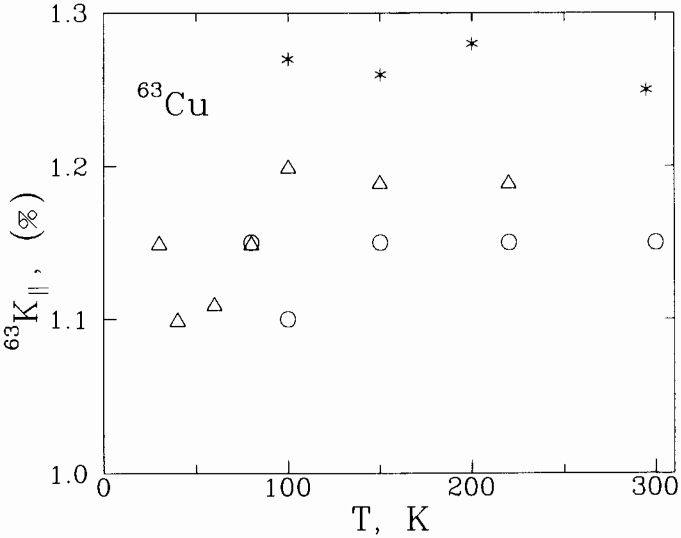

Fig.1. The total magnetic shift of Copper (Cu2 sites) as a function of temperature with $\vec{H} \parallel \vec{c}$ in $YBa_2Cu_3O_{6.9}$ for different disordering due to the fast neutron fluxes: (*) — $\varphi = 0$; (○) — $\varphi = 5 \cdot 10^{18}\ \mathrm{cm}^{-2}$; (Δ) — $\varphi = 1.2 \cdot 10^{19}\ \mathrm{cm}^{-2}$.

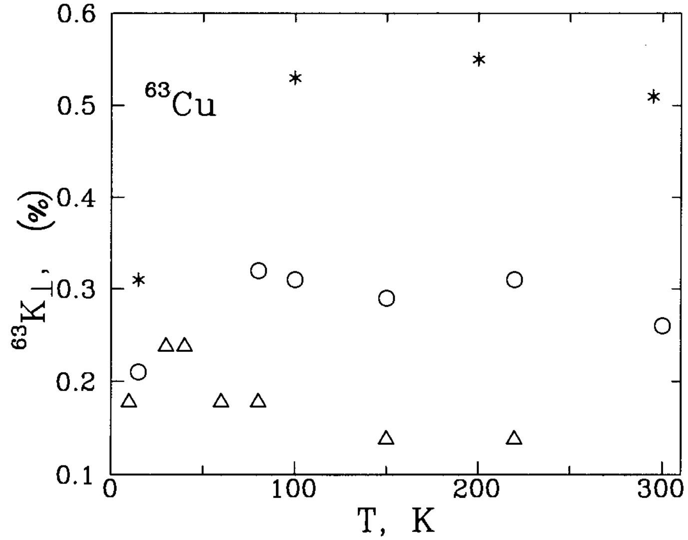

Fig.2. The total magnetic shift of Copper (Cu2 sites) as a function of temperature with $\vec{H} \perp \vec{c}$ in $YBa_2Cu_3O_{6.9}$ for different disordering due to the fast neutron fluxes: (*) – $\varphi = 0$; (○) – $\varphi = 5 \cdot 10^{18}$ cm^{-2}; (Δ) – $\varphi = 1.2 \cdot 10^{19}$ cm^{-2}.

ferred interaction B of the nearest-neighbor copper spins $\vec{S}_i$ with resonant nuclei $\vec{I}$ in the Hamiltonian proposed by Milla and Rice [14] for the planar Cu site:

$$\mathcal{H} = {}^{63}\gamma \cdot \hbar \cdot \vec{I}\Big(\vec{A} \cdot \vec{S} + \sum_{i=1}^{4} B \cdot \vec{S}_i\Big). \tag{3}$$

As can be seen in the figures, both NMR shifts $^{63}K_\parallel$ and $^{63}K_\perp$ decrease substantially with neutron flux. Moreover, $^{63}K_\perp$ increases with decreasing temperature for the most disordered sample ($\varphi = 1.2 \cdot 10^{19}$ cm^{-2}), which is about to become nonsuperconducting under stronger irradiation. The total ^{63}Cu NMR magnetic shift consists of two parts:

$$^{63}K_{\parallel(\perp)} = K_S + K^L_{\parallel(\perp)}, \tag{4}$$

$$K_S = \frac{1}{\mu_B}(A_\parallel + 4B)\chi_S. \tag{5}$$

The spin contribution K_S is supposed to be isotropic. The second anisotropic contribution, $K^L_{\parallel(\perp)}$, is determined by the Van Vleck paramagnetism of the 3d-shells of copper:

$$K^{L}_{\alpha\alpha} = 4\mu_B^2\langle\frac{1}{r^3_{3d}}\rangle\sum_{n}\frac{|\langle 0|\hat{L}_{\alpha}|n\rangle|^2}{E_n - E_0} = 2\mu_B\langle\frac{1}{r^3_{3d}}\rangle\chi^{VV}_{\alpha\alpha}\,. \qquad (6)$$

As has been shown [13] for $YBa_2Cu_3O_7$, the Van-Vleck susceptibility $\chi^{VV}_{\alpha\alpha}$ depends on the position of unoccupied ^{63}Cu 3d orbitals d_{xy}, d_{xz} relative to the nearly filled orbital $d_{x^2-y^2}$, which is located near the Fermi energy.

In order to separate the spin and the orbital contributions to the total NMR line shift, we used results of the NMR line shift measurements in the superconducting state. As is known for a non-irradiated $YBa_2Cu_3O_7$ sample, the value of $^{63}K_{\parallel}$ does virtually not change below T_c, whereas ^{63}K decreases markedly for $T < T_c$. This different behavior is due to mutual cancellation of the overall hyperfine magnetic field for the case $\vec{c} \parallel \vec{H}_0$ due to the negative on-site contribution $A_{\parallel} \simeq 160$ kOe/μ_B and the transferred hyperfine interaction B from four nearest Cu atoms [12,13]. Our data show that this situation persists for irradiated samples of $YBa_2Cu_3O_7$.

This leads us to conclude that the decrease of $^{63}K_{\parallel}$ in heavily irradiated $YBa_2Cu_3O_{6.9}$ ($\varphi = 1.2 \cdot 10^{19}$ cm^{-2}) is due to the variation of $\chi_{\parallel}^{VV}$. Using results for the energy level arrangement of a 3d^9 ion in the planar Cu2-positions, the authors of [13] note that the ratio $K^{L}_{\parallel}/K^{L}_{\perp} = 4$, which is close to the measured value in $YBa_2Cu_3O_7$ can be obtained for $\varepsilon_{xy} = 2$ eV and $(\varepsilon_{xy}, \varepsilon_{yz}) = 2.2$ eV above the ground state $\varepsilon_{x^2-y^2}$. As can be seen, the value of this ratio does not change for $YBa_2Cu_3O_7$ ($\varphi = 5 \cdot 10^{18}$ cm^{-2}) in which a metallic type conductivity ($\varrho \sim T$) persists. However, for a sample with $\varphi = 1.2 \cdot 10^{19}$ cm^{-2}, where a sufficient growth in the hopping contribution to conductivity was found, we obtain a sharp decrease in $K^{L}_{\perp}$. This incre-

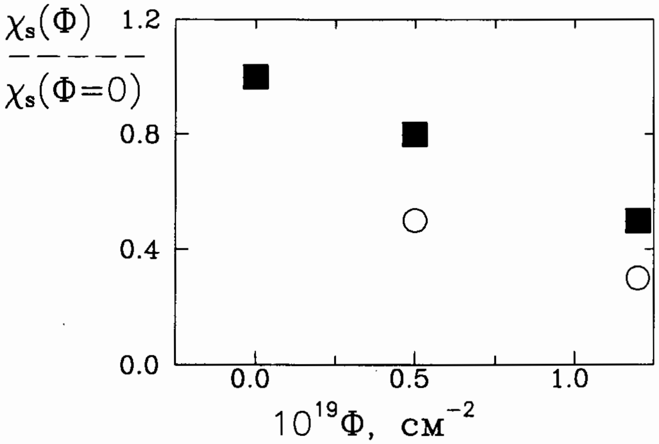

Fig.3. Spin susceptibility χ_{σ} of $YBa_2Cu_3O_{6.9}$ versus fast neutron flux: (○) – Copper NMR shift data; (■) – Yttrium NMR shift data.

ases the ratio $K_{\parallel}^{L}/K_{\perp}^{L}$ and may indicate an additional shift of the excited xy and yz states under irradiation, because virtual transitions between the ground state x^2-y^2 and these states do not contribute to $K_{\parallel}^{L}$.

The magnitude of the uniform spin susceptibility χ_S $(q \simeq 0)$ was obtained from measurements of $\Delta K_{\perp} = K_{\perp}(T \simeq T_c) - K(T \simeq 4\ \mathrm{K})$. The variation of $\chi_S(\varphi)/\chi_S$ $(\varphi = 0)$ the neutron flux is shown in Fig.3. Since the fundamental contribution to χ_S is due to Pauli paramagnetism [6], we may conclude that a sharp decrease in the density of states, DOS, near the Fermi level accompanies the appearance of a structural disorder in $YBa_2Cu_3O_{6.9}$. At present, it is difficult to formulate a simple reason for such behavior of the DOS under disordering in $YBa_2Cu_3O_{6.9}$. It may be caused by a smearing of the Van Hove singularity near the Fermi energy in ordered $YBa_2Cu_3O_{6.9}$ as is proposed in some publications. Another case, which may be taken into consideration, is the appearance of a "pseudo gap" at the Fermi energy due to the interplay of the disorder and the electron correlation effects as discussed in [16]. Such a situation is typical for strongly correlated electron systems, which are close to the metal-insulator transition due to disordering [16].

3.2. Spin-Lattice Relaxation Rate of ^{63}Cu

Measurements of the ^{63}Cu spin-lattice relaxation rate were made at the NQR frequencies of planar copper (Cu2 positions) [10]. In the normal state, the recovery of the ^{63}Cu spin echo amplitude was satisfactorily described by the relation $A_t = A_0(1 - \exp(-t/T_1))$. For $T < T_c/2$, however, the recovery after saturation was not described by this single exponential dependence. The spin-lattice relaxation rate ^{63}R data quoted for this temperature region correspond to the slowly changing part of the recovery curve following the saturation r.f. pulse comb. In the entire temperature region, the spin-lattice relaxation is determined by fluctuations of the magnetic hyperfine field produced by the exchange-coupled spin excitations of ^{63}Cu neighboring atoms [2,3]. At helium temperatures, ^{63}R approaches a constant value which increases with neutron flux. We supposed [10] an additional temperature independent channel of relaxation that manifests itself at low temperatures in disordered samples of $YBa_2Cu_3O_{6.9}$. Such temperature independent behavior takes place when the spin-lattice relaxation process is monitored by the paramagnetic localized magnetic moments in CuO_2 planes under spin diffusion conditions. This proposal may be proved by our results reported earlier in [10]. Here we recall the major facts that support this supposition. Firstly, in irradiated samples with $\varphi > 1 \cdot 10^{19}\ \mathrm{cm}^{-2}$, we have found a drastic decrease of the NQR line intensity of copper in the CuO_2 plane, whereas the NQR line intensity of copper in the chain remains nearly unchanged. Secondly, the Curie like contribution $C/(T-\Theta)$ $(\Theta < 5\ \mathrm{K})$ appears in the temperature dependence of the magnetic susceptibility in irradiated samples.

The value of the Curie constant increased in proportion to the flux and reached $C(2 \cdot 10^{19}\ \mathrm{cm}^{-2}) = 0.075\mathrm{cm}^3 \cdot \mathrm{K/mol}$. By taking $\mu_{\mathrm{eff}}(\mathrm{Cu}) \simeq 0.6\mu_B$, we evaluated the mean distance between localized moments in the $YBa_2Cu_3O_{6.9}$ sample ($\varphi = 2 \cdot 10^{19}\ \mathrm{cm}^{-2}$) as $(2-3)a$ where a is the lattice parameter.

Spin-lattice relaxation data ${}^{63}R(T)$ after subtraction of ${}^{63}R(T = 4.2\ \mathrm{K})$ are shown in Fig.4. Above $T = 100$ K, the value of ${}^{63}R$ decreases with increasing neutron flux. In irradiated samples, the relaxation data below $T = 100$ K can satisfactorily be described with a power law temperature dependence: ${}^{63}R \sim T^{(1.3 \pm 0.3)}$. As the temperature is raised further, ${}^{63}R(T)$ increases at a slower rate. For a flux of $\varphi = 1.2 \cdot 10^{19}\ \mathrm{cm}^{-2}$ the ^{63}Cu spin-lattice relaxation rate becomes approximately independent of temperature above $T_c = 200$ K. A similar growth of the temperature derivative of ${}^{63}R(T)$ with decreasing temperature has been found in oxygen depleted $YBa_2Cu_3O_{6.63}$ [3,4]. The kink in the temperature dependence has been attributed by the authors of [6] to a substantial decrease in the uniform spin

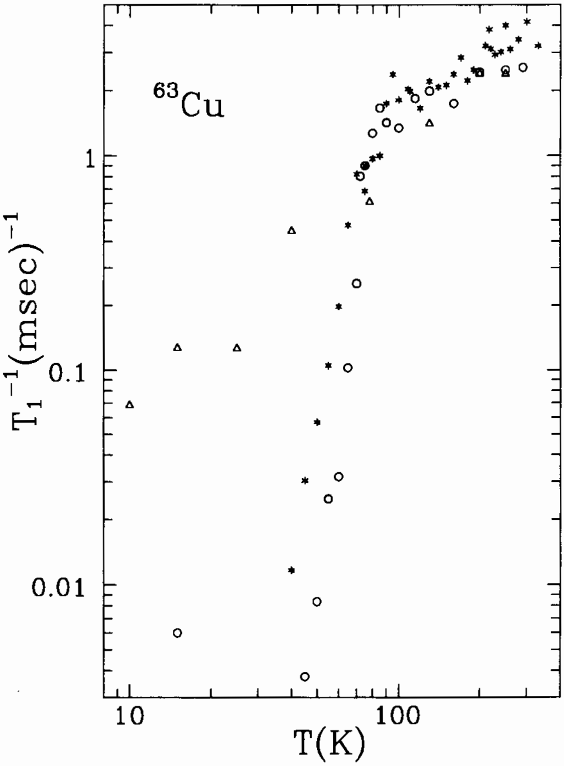

Fig.4. The temperature dependence of the ^{63}Cu spin-lattice relaxation rate ${}^{63}R(T)-{}^{63}R(T = 4.2\ \mathrm{K})$ of $YBa_2Cu_3O_{6.9}$ for different fast neutron fluxes: (*) — $\varphi = 0$; (○) — $\varphi = 5 \cdot 10^{18}\ \mathrm{cm}^{-2}$; (Δ) — $\varphi = 1.2 \cdot 10^{19}\ \mathrm{cm}^{-2}$. The relaxation measurements were made at the NQR frequencies at zero magnetic field [10].

susceptibility below T~150 K. In the case of disordered $YBa_2Cu_3O_{6.9}$ ($\varphi = 5 \cdot 10^{18}$ cm^{-2}), χ_S is nearly independent of temperature, as can be seen from the measurements of ^{63}K in the normal state. Moreover, for sample $\varphi = 1.2 \cdot 10^{19}$ cm^{-2} we note a slight increase in spin susceptibility when the temperature is lowered.

As stated above, the peculiarities of the ^{63}Cu spin-lattice relaxation in CuO_2 planes are determined mainly by magnetic fluctuations of the antiferromagnetically coupled spins whose spatial correlation may be characterized by the magnetic correlation length ξ_m. Below we use the "antiferromagnetic" Fermi liquid model proposed in [6], to discuss our results. By use of the Hamiltonian (3), the following expression can be derived for the spin-lattice relaxation rate of copper in the CuO_2 plane [6].

$$\frac{1}{3}\,{}^{63}R_{\mathrm{NQR}} = {}^{63}R_{\parallel\mathrm{NMR}} \sim \chi_S(q=0)\,T(a + b\xi_m^2)\,. \tag{7}$$

The first term in Eq.(7) describes mainly a channel of relaxation via delocalized electron (or hole) states, the so-called Korringa relaxation. The second term is introduced to describe the influence of the enhanced short-wave spin correlation in the dynamic spin susceptibility $\chi_S(q,\omega \simeq \omega_{\mathrm{NMR}})$ near the antiferromagnetic peak $q \simeq Q_{\mathrm{AF}} = (\pi/a;\pi/a)$.

The quantity $^{63}R(\varphi)$ should be proportional to $\chi_S(\varphi)$ if the expression in the brackets of Eq.(7) does not change. Our results show a slower decrease in the spin-lattice relaxation rate of copper, as compared with the sharp decrease of the uniform spin susceptibility due to disordering. Allowing for the magnetic correlation length to increase with disordering, one could understand, following Eq.(7), the different rates of decrease for $R(\varphi)$ and χ_S. In this case ξ_μ would increase in the sample with $\varphi = 1.2 \cdot 10^{19}$ cm^{-2} by nearly a factor of 2 as compared with the non-irradiated $YBa_2Cu_3O_{6.9}$. A similar analysis for oxygen depleted $YBa_2Cu_3O_{6.63}$ [4,6] shows that reducing the oxygen content increases ξ_m. This phenomenon may be due to weakening of the influence of the hole screening on the Cu—O—Cu interaction when the concentration of holes is decreased. An appearance of a spatial hole localization in the CuO_2 plane due to the structural disorder may be discussed as another cause of the increase of ξ_m. This case is more preferable for metallic systems with disorder. More direct evidence for this supposition can be derived from spin-lattice relaxation experiments on oxygen, whose electronic p states provide the conductivity in CuO_2 planes.

3.3. NMR Line Shift and Spin-Lattice Relaxation Rate of Yttrium in the Normal State

The ^{89}Y NMR shift data of irradiated $YBa_2Cu_3O_{6.9}$ for the normal state are shown in Fig.5. For a non-irradiated sample, the NMR shift of yttrium

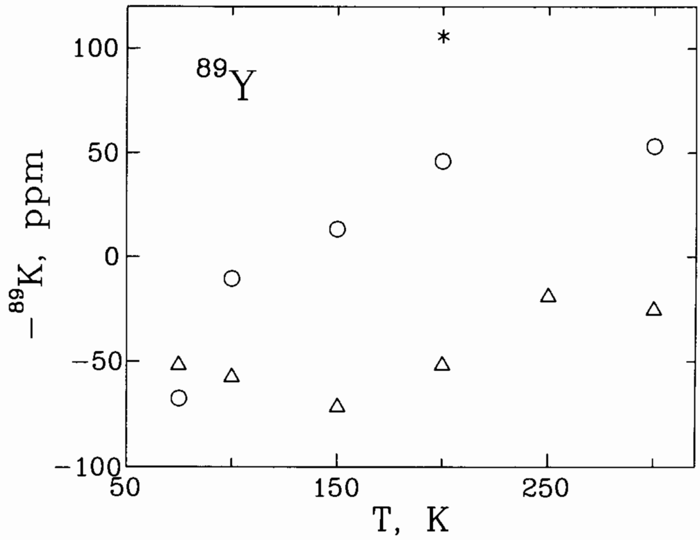

Fig.5. ^{89}Y NMR shift of $YBa_2Cu_3O_{6.9}$ referenced to YCl_3 as a function of temperature for different fast neutron fluxes: (*) — $\varphi = 0$; (○) — $\varphi = 5 \cdot 10^{18}$ cm^{-2}; (Δ) — $\varphi = 1.2 \cdot 10^{19}$ cm^{-2}.

$^{89}K = -70(20)$ ppm is independent of temperature, in accord with the results reported in [5].

In disordered samples, an additional broadening of the ^{89}Y NMR line gives rise to an error in the measurement of the yttrium NMR shift. The absolute value of ^{89}K decreases when the temperature is lowered. The temperature dependence of ^{89}K in irradiated samples repeats, mainly, the ^{89}Y NMR line shift behavior in an oxygen depleted $YBa_2Cu_3O_{7-\delta}$ with nearly the same T_c. For comparison, we have shown in Fig.5 Alloul's results [5] for $\delta = 0.15$ ($T_c = 80$ K) and $\delta = 0.49$ ($T_c = 40$ K). The peculiarities of the ^{89}Y NMR line shift in $YBa_2Cu_3O_{7-\delta}$ have been discussed in detail by Alloul *et al.* [5]. The total ^{89}Y NMR line shift consists of the Knight shift $^{89}K_S$ and the chemical shift $^{89}K_{CS}$:

$$^{89}K = {}^{89}K_S + {}^{89}K_{CS}\,. \tag{8}$$

The first part in Eq.(8) should be proportional to the uniform spin susceptibility χ_S ($q = 0$). The negative value of K_S is due to effects of the exchange core polarization by electrons of the molecular orbital Cu(3d)—O(2pσ) that transfer the non-zero spin density to Y [5]. As is known, this interatomic electron binding is widely discussed in models of the electron structure for cuprates with perovskite layers. The ^{89}K value depends on the spin contribution of the oxygen states at the Fermi level. This conclusion will be correct as long as we are sure that the spatial part of this molecular orbital and the Y chemical shift do not change under irradiation.

Assuming that the second part in Eq.(8) is independent of temperature, we fix the value of $^{89}K_{CS}$ to be (− 0.03 %) [20] for all fluxes in the following. An investigation of crystal fields for the rare-earth ions Ho^{3+} and Er^{3+} in irradiated $HoBa_2Cu_3O_7$ and $ErBa_2Cu_3O_7$ [15] give some proof for this supposition. These authors have found that the nearest charge environment of ions and the scale of their hyperfine splitting does not change under radiation-induced disorder. If this situation holds for yttrium in irradiated $YBa_2Cu_3O_{6.9}$, i.e., a displacement of the covalent energy levels is absent, then we can expect K_{CS} to be constant.

Therefore we will assume that the variation of ^{89}K via the flux is due to a decrease in the spin susceptibility in irradiated $YBa_2Cu_3O_{6.9}$. The variation of $\chi_S(\varphi)$, derived from the Y NMR line shift data for $T = 300$ K, is shown in Fig.3. As can be seen, the Y NMR line shift data give a slower decrease of $\chi_S(\varphi)$ than the one obtained from $^{63}K_\perp$ measurements. We can indicate two possible reasons for this difference. First, the transferred hyperfine field on Y may change under disorder. Second, we cannot exclude a possible spin density redistribution for small q in disordered samples. Some proof for the latter case may be obtained from NMR experiments on planar oxygen. In our view, we can also have a confirmation for the second supposition by analyzing the ^{89}Y spin-lattice relaxation rate data of ^{89}R which are shown in Fig.6.

For the normal state, the ^{89}R data can be satisfactory described by the linear dependence where the slope increases with flux. Such a temperature depen-

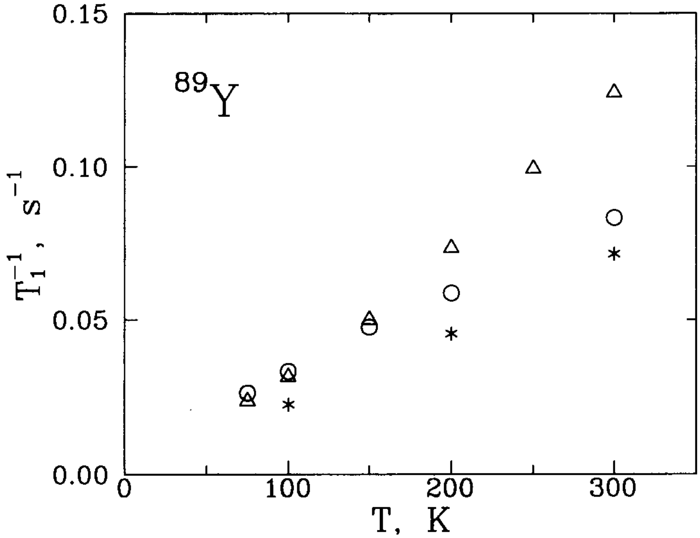

Fig.6. ^{89}Y spin-lattice relaxation rate of $YBa_2Cu_3O_{6.9}$ as a function of T for different fast neutron fluxes: (*) − $\varphi = 0$; (o) − $\varphi = 5 \cdot 10^{18}$ cm^{-2} ; (Δ) − $\varphi = 1.2 \cdot 10^{19}$ cm^{-2}.

dence holds for the relaxation process due to an interaction with electrons in the conduction band. This Korringa process leads to $^{89}R \sim \chi_S^2$:

$$^{89}R = z \cdot 2\gamma^2 \cdot hk_B \cdot TH_{CT}^2 \left(\frac{\chi_S}{2\mu_B^2}\right)^2 = z \cdot 2\gamma^2 \cdot hk_B \cdot TH_{CT}^2 \cdot N^2(E_F) \qquad (9)$$

with z being the number of nearest neighbor oxygen atoms whose magnetic hyperfine field fluctuations provide the spin-lattice relaxation of ^{89}Y. Taking into consideration the decrease of χ_S with φ, it is difficult to analyze the cause of the measured increase of ^{89}R in disordered $YBa_2Cu_3O_{6.9}$. It should be born in mind that expression (9) has been derived in the limit of short electron correlation times in the conduction band, i.e. $\omega_0 t_c \ll 1$ ($\omega_0 = \gamma B_0$). The electron correlation time τ_c is approximately the time for an electron with $V = V_F$ to cross the nearest neighbor interatomic distance a:

$$\tau_c \simeq \frac{a}{V_F} \simeq \hbar N(E_F)\,. \qquad (10)$$

In our opinion, we have a case similar to the situation discussed earlier by Warren [17] who observed the anomalous growth of the spin-lattice relaxation rate in In_2Te_3 in the region of temperatures where electron localization effects turn out to be essential.

Following [17], one can modify Eq.(9) by taking into account the possibility for τ_c to deviate from the predicted value Eq.(10) for a nearly free electron gas:

$$^{89}R_{\mathrm{Korr.}} = z\frac{^{89}\gamma^2\hbar k_B}{2\mu_B^2}\,{}^{89}K_S^2\,T\frac{\tau_c}{\hbar N(E_F)} = z\frac{^{89}\gamma^2\hbar k_B}{2\mu_B^2}\,{}^{89}K_S^2\,T\eta\,. \qquad (11)$$

Here Warren's relaxation factor $\eta = \tau_c\,/\hbar N(E_F)$ shows an increase of ^{89}R with respect to the Korringa rate. Thus we have related the ^{89}Y spin-lattice relaxation rate enhancement in irradiated $YBa_2Cu_3O_{6.9}$ to an increase in electron correlation time. For the most disordered sample, this leads to the ratio $\tau_c(\varphi = 1.2 \cdot 10^{19}\ \mathrm{cm}^{-2})/\tau_c(\varphi = 0) = 5(1)$. For the metallic phase, the relaxation rate enhancement factor can be expressed in terms of the electrical conductivity, σ [18,19]. The Korringa-like temperature dependence of ^{89}R gives additional support for the application of Eq.(11) to irradiated $YBa_2Cu_3O_{6.9}$

$$\eta(\varphi) = \frac{R(\varphi)}{R_{\mathrm{Korr.}}} \simeq \left(1 + \frac{\pi}{3}\frac{\sigma_c^2}{\sigma(\sigma + \sigma_c)}\right). \qquad (12)$$

Table.

YBa$_2$Cu$_3$O$_{6.9}$

φ, 10^{18} cm^{-2}	σ, $(\Omega \cdot \mathrm{cm})^{-1}$ [8]		$^{89}\eta(\varphi)/^{89}\eta(\varphi = 0)$	η(calc.(12), $T = 300$ K)		$\eta(\varphi)/\eta(\varphi = 0)$
	$T = 100$ K	$T = 300$ K	$T = 300$ K	$\sigma_c = 10^3$ $(\Omega \cdot \mathrm{cm})^{-1}$	$\sigma_c = 250$ $(\Omega \cdot \mathrm{cm})^{-1}$	$\sigma_c = 250$ Ω/cm^{-1}
0	2.50	1.00	1.0	1.2	1.05	1.00
5	0.50	0.33	1.2	2.3	1.37	1.30
12	0.17	0.18	1.7	6.0	1.78	1.71

Here σ_c is the so-called minimum metallic conductivity [20]. By summarizing different estimates, we get a rather large window, $\sigma_c = (100 \div 1000)(\Omega \cdot \mathrm{cm})^{-1}$. Further, we can set $\sigma(\omega) = \sigma(\omega = 0)$ in Eq.(12). It is interesting to compare the ^{89}Y relaxation data with results of σ measurements [8] which have been made in the same irradiated samples of YBa$_2$Cu$_3$O$_{6.9}$. As reported in [8], metallic conductivity ($\mathrm{d}\sigma/\mathrm{d}T < 0$) has been found to exist in all the samples that we use in our study for $T > 100$ K. In Table, we present values of σ for the lowest temperature ($T = 100$ K) and room temperature [8], at which metallic conductivity dominates over the hopping contribution. The values of η derived from ^{89}Y spin-lattice relaxation rate measurements and by using Eq.(12) with different σ_c are also listed in Table. As can be seen, the best fit is found for $\sigma_c = 250(30)(\Omega \cdot \mathrm{cm})^{-1}$. This σ_c value does not contradict the estimated values derived in numerous papers concerning the problem of Anderson's localization.

Obviously, it would be interesting to measure the ^{89}Y spin-lattice relaxation rate in a sample with a greater flux. Data thus obtained would permit us to verify the applicability of Eq.(12) to a region with a greater degree of disorder. According to [19], this expression must hold up to the region in the proximity of the metal-insulator transition due to disorder. It may be shown [19] that at the dielectric side of this transition the Warren relaxation factor can be expressed in terms of the Fermi momentum p_{F} and the localization length R_{loc}.

$$\eta \cong p_{\mathrm{F}} R_{\mathrm{loc}} \,. \tag{13}$$

As predicted in [19], the maximum value of η would be reached at the point of this transition. As we move into the dielectric phase a decrease of $^{89}\eta$ can occur due to an increase of disorder. Indeed in Anderson's dielectric phase, electrons (or holes) are localized within a sphere with $R \sim R_{\mathrm{loc}}$. With increasing disorder R_{loc} would drop. This decrease would lead to a less effective interaction with ^{89}Y, and, as a consequence, a decrease of $^{89}\eta$ would be observed. But we do not rule out the possibility that another contribution, which can appear in disordered samples will mask this bending of $\eta(\varphi)$.

4. Conclusion

The ^{63}Cu and ^{89}Y data reported in this paper, for radiationally disordered $YBa_2Cu_3O_{6.9}$ can be summarized as follows:

- an increase of disorder is accompanied by a sharp decrease of the uniform spin susceptibility and by a growth of the antiferromagnetic spin correlation length in CuO_2 planes.
- an increase of the ^{89}Y spin-lattice relaxation rate with neutron flux gives evidence for a spatial redistribution of spin density in CuO_2 layers that is due to the occurrence of electron localization effects under irradiation.

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