NMR spectra of ^{205}Tl in the high-temperature superconductors $Tl_2Ba_2Ca_nCu_{n+1}O_{6+2n}$ with $n=0, 1, 2$

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(Submitted 16 November 1989)
Pis'ma Zh. Eksp. Teor. Fiz. **51**, No. 1, 32–34 (10 January 1990)

The NMR spectra of ^{205}Tl in the high-temperature superconductors $Tl_2Ba_2Ca_nCu_{n+1}O_{6+2n}$ ($n = 0, 1, 2$) in the normal state have been studied. It is shown that the additional line observed in the spectra of compounds with $n = 1$ and $n = 2$ may be due to a partial replacement of calcium by thallium in these systems.

Among high-temperature superconductors with a perovskite-like structure discovered thus far, considerable attention is focused on the study of compounds of the type $Tl_2Ba_2Ca_nCu_{n+1}O_{6+2n}$ ($n = 0, 1, 2$). The temperature of the superconducting transition for these systems increases with n and for the system with $n = 2$ can reach 125 K (Ref. 1). The tetragonal structure of these compounds is formed by alternating metal-oxygen planes (Fig. 1), with the Tl-O layers arranged in pairs, and in layers where the metal is Ca, oxygen atoms are absent.[2–4] For compounds with such a complex structure, the probability of formation of various structural disarrangements is high. In particular, atoms of one kind can occupy positions of atoms of another kind. To clarify this possibility, we made a study of nuclear magnetic resonance spectra of ^{205}Tl in the compounds $Tl_2Ba_2Ca_nCu_{6+2n}$ with $n = 0, 1, 2$. The presence of thallium in the structure makes these systems very convenient for study by the NMR method, since both natural isotopes ^{205}Tl and ^{203}Tl have spin of 1/2, and therefore, there is no line broadening due to quadrupole effects.

To synthesize the samples, we used the corresponding metal oxides Tl_2O_3, BaO, CaO, and CuO. The synthesis was carried out at 840–860 °C during a time ranging from 10 min to 2 h in air, with subsequent rapid cooling. After the synthesis, the samples were checked by x-ray diffraction analysis. The structural parameters of the samples and the T_c values, determined by the induction method, are listed in Table I. The NMR experiments were carried out with a pulsed spectrometer. The spectra were recorded by measuring the intensity of the spin echo signal as a function of the magnetic field (Clark's method[5]) at 22 150 kHz.

Figure 2 shows the NMR spectra of ^{205}Tl for all three compounds studied at temperatures surpassing the corresponding T_c values by a few degrees. All the spectra were recorded with a 38-μsec delay between the pulses that formed the echo. As is evident from Fig. 2 in the case of the compound with $n = 0$, a single asymmetric line is observed. For the compound with $n = 1$, the spectrum shows two lines. One of them (Tl–1) is similar in position and shape to the line in the spectrum of the compound with $n = 0$. Moreover, to the right of Tl–1 there is an additional line Tl–2. The spectrum for the compound with $n = 2$ also has a similar appearance, but in this case,

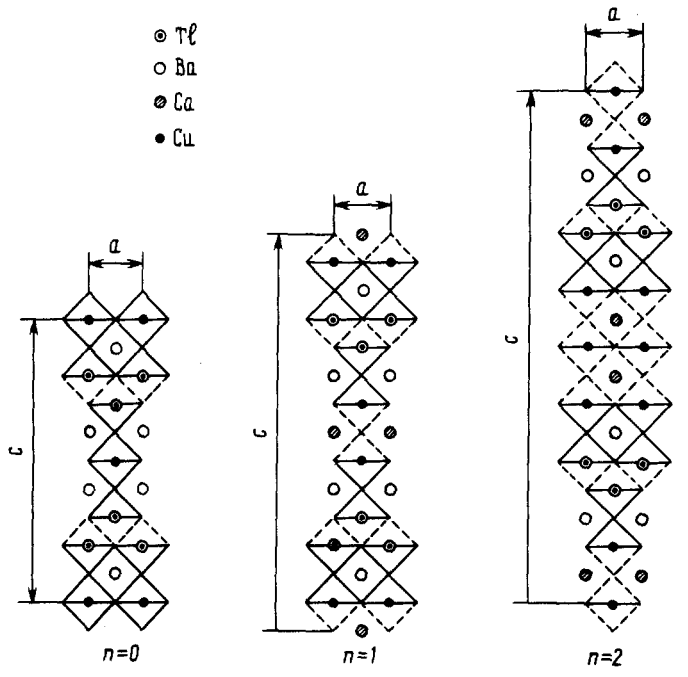

FIG. 1. Structures of the compounds $Tl_2Ba_2Ca_nCu_{n+1}O_{6+2n}$ $n = 0, 1, 2$.

the T1–2 line is broader. The line shifts were determined relative to the value $^{205}\gamma/2\pi = 2.4567$ kHz/Oe and are listed in Table I.

The line in the spectrum of the compound with $n = 0$, and also the T1–1 lines for the compounds with $n = 1$ and $n = 2$, should correspond to the thallium atoms in the Tl-O layers in these systems. The asymmetric shape of these lines is probably due to the shear anisotropy for this position, which has axial symmetry. The T–2 lines for systems with $n = 1$ and $n = 2$ are apparently determined by some other position of the thallium atoms in these systems. Fugiwara *et al.*,[6] who first studied NMR on thallium nuclei in the system with $n = 1$, postulated that this line is due to the position of thallium in Tl-O layers, and next to this position an oxygen vacancy is located. Along with this hypothesis, Ref. 7 discusses the possibility of partial replacement of calcium

TABLE I.

Composition	a, Å	c, Å	T_c, K	K_1, %	K_2, %
$Tl_2Ba_2CuO_{6-\delta}$	3.87	23.20	88	0.30 (2)	–
$Tl_2Ba_2CaCu_2O_{8-\delta}$	3.86	29.26	108	0.25 (2)	– 0.15 (2)
$Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$	3.85	35.57	117	0.28 (2)	– 0.10 (3)

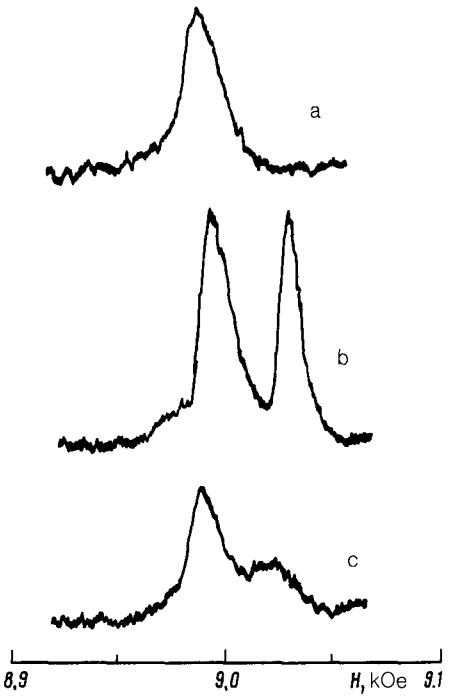

FIG. 2. NMR spectra of ^{205}Tl in the compounds $Tl_2Ba_2Ca_nCu_{n+1}O_{6+2n}$ at a frequency of 22 150 kHz. a—$n = 0$, $T = 29$ K; b—$n = 1$, $T = 120$ K; c—$n = 2$, $T = 120$ K.

by thallium in this compound. Results of structural studies[3,4] also support this possibility. In our case, as is evident from the figure, for the system with $n = 0$, where the position of calcium is generally absent, the Tl–2 line is not observed. This may be regarded as a confirmation of the possibility of partial replacement of calcium by thallium in systems with $n = 1$ and $n = 2$.

Such an interpretation of the Tl–2 line may also be supported by the fact that the times of transverse relaxation for the Tl–1 and Tl–2 lines in these systems are substantially different. Thus, for the compound with $n = 1$, T_2(Tl–1) $= 30 \pm 10$ μsec, and T_2(Tl–2) $= 110 \pm 30$ μsec at 120 K. The situation is similar in the case of the compound with $n = 2$. During the preparation of this publication, we learned that a similar result for these systems was obtained by Zhdanov *et al.*[8] This effect is also related to the fact that the intensities of the Tl–1 lines in spectra b and c shown in Fig. 2 are low compared to the intensities of the corresponding Tl–2 lines, since the spin echo signal for Tl–1 decays considerably faster than for Tl–2. As we know, the transverse relaxation time is determined primarily by the interaction between nuclear spins (dipole-dipole and indirect interaction). The main contribution to the transverse relaxation of the spins of ^{205}Tl in Tl–O layers is apparently due to indirect exchange with spins of other natural thallium isotope, ^{203}Tl [as in the case of the compound Tl_2O_2 (Ref. 9)]. Therefore, the essentially high value of T_2 for Tl–2, as compared to Tl–1,

may be due to the absence of other thallium atoms in the nearest neighborhood of this position, as in the case of the position of calcium.

The partial replacement of calcium by thallium in the structure of the compounds $Tl_2Ba_2Ca_nCu_{n+1}O_{6+2n}$ with $n = 1$ and $n = 2$ can have an appreciable effect on the properties of these systems. In particular, as a result of such substitution, because of the difference in the valances of thallium and calcium, a change in the number of holes in Cu–O layers is possible, and this should affect the value of T_c in these systems. Another possibility is discussed in Ref. 8, which shows that the shift of the Tl–2 line in compounds with $n = 1$ and $n = 2$ correlates well with the temperature-dependent part of the magnetic susceptibility of these systems, which follows the Curie–Weiss law. This enabled Zhdanov *et al.*[8] to postulate that the replacement of calcium by thallium can induce a magnetic moment of the nearest copper atoms, which in turn will lead to an additional shift at the Tl nucleus in this position. It is of interest to note here that, as was shown by our measurements, the susceptibility of the compound $Tl_2Ba_2CuO_6$ is nearly independent of temperature in the normal state and amounts to 2.7×10^{-6} cm^3/g at 300 K.

The authors are very grateful to I. A. Kuz'min for help in the preparation and adjustment of the pulsed NMR spectrometer, and to S. V. Verkhovskiĭ for letting us know the results of Ref. 8 prior to publication and for helpful discussions.

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Translated by A. Peiperl