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NMR and NQR study of Ca-substituted superconducting $YBa_2Cu_4O_8$

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We report a set of nuclear quadrupole resonance (NQR) measurements including a spin-echo double-resonance (SEDOR) experiment which provides convincing evidence that the additional chain Cu NQR line in Ca-substituted $YBa_2Cu_4O_8$ does stem from chain Cu sites disturbed by the "impurity" Ca ions. From an analysis of signal intensities we conclude that "impurity" Ca ions, responsible for the additional line, substitute Y^{3+}. At high Ca doping, the concentration of the substituted Y sites, x', is appreciably smaller than the nominal Ca concentration, x. Since it is x' which is responsible for a direct increase of the hole charge-carrier concentration, n, effects connected with the increase of n such as the planar Cu spin-lattice relaxation rate, the NQR frequency, and the magnetic shift are only weakly dependent on x. Thus, the substantial increase of T_c with x suggests that, besides the increase of n, other effects have to play a role in the T_c enhancement. One such effect might be the opening of the spin pseudogap. At 150 K, both the main and additional Cu NQR lines in nominal $YBa_{1.9}Ca_{0.1}Cu_4O_8$ show distinctly anomalies not seen in pure $YBa_2Cu_4O_8$ that point out the Ca doping induced structural phase transition recently observed in specific-heat, elastic-neutron-scattering, and x-ray-diffraction measurements.

I. INTRODUCTION

The superconducting transition temperature T_c of the partially Ca-substituted $YBa_2Cu_4O_8$ increases from about 81 K up to 91 K.[1,2] The highest T_c is achieved in compounds with nominal chemical composition $YBa_{1.9}Ca_{0.1}Cu_4O_8$ (Ref. 3) or $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$.[1] To understand this substantial T_c enhancement it is crucial to know which of the two different ions, Y^{3+} or Ba^{2+} the Ca^{2+} is substituting. Recently, we had intensively investigated this problem by Cu nuclear quadrupole resonance (NQR).[3] Based on the analysis of an "additional" chain copper Cu(1) NQR line, which appears through Ca substitution, we concluded that the major fraction of Ca occupies the Ba site. A similar conclusion was reached on grounds of electron-energy-loss investigations,[2] which have shown almost no change of hole carrier concentration in Ca-substituted $YBa_2Cu_4O_8$ as compared to the pure compound implying that Ca^{2+} is replacing the isovalent Ba^{2+}.

From other investigations,[4] however, it is known that in contrast to the Ca substitution, the Sr^{2+} replacement of the isovalent Ba^{2+} does not change T_c at all. Another argument against the substitution of Ba^{2+} by Ca^{2+} is their big difference in size. If the involved ionic radii $r_{Ba^{2+}}$ (1.42 Å), $r_{Sr^{2+}}$ (1.26 Å), $r_{Ca^{2+}}$ (1.12 Å) and $r_{Y^{3+}}$ (1.02 Å) are compared one notices that while $r_{Ba^{2+}}$ and $r_{Sr^{2+}}$ are still somewhat compatible, the mismatch between $r_{Ba^{2+}}$ and $r_{Ca^{2+}}$ could pose a problem, such that one would rather expect the Ca ion replacing the more matching Y instead of the huge Ba ion. In addition, by Ca^{2+} replacing Y^{+3} the charge carrier concentration in the CuO_2 planes would increase thus explaining in a natural way the T_c enhancement of the originally underdoped $YBa_2Cu_4O_8$.

In a number of recent investigations[5–7] there is growing evidence that Ca potentially substitutes Y rather than Ba in $YBa_2Cu_4O_8$. To reconcile the opposite views concerning the site Ca occupies in $YBa_2Cu_4O_8$ we decided to revisit the problem by performing new NQR, nuclear magnetic resonance (NMR) as well spin-echo double-resonance (SEDOR) experiments in old and new Ca-substituted $YBa_2Cu_4O_8$ samples. We were also stimulated by recent observations of anomalies in the elastic constant and the specific heat,[8] and in the temperature dependence of lattice parameters[9,10] around $T' = 150$ K in Ca^{2+}-substituted $YBa_2Cu_4O_8$, that are possibly caused by a second-order structural phase transition, even though there is no change observed in crystal symmetry.[9]

II. EXPERIMENT

The samples were prepared by heating up to 1000 °C under high oxygen pressure[11] a mixture of oxides with nominal chemical composition $YBa_{2-x}Ca_xCu_4O_8$ ($x = 0$, 0.02, 0.05, 0.1). X-ray diffraction revealed a single-phase polycrystalline material without observable traces of $YBa_2Cu_3O_7$ or $Y_2Ba_4Cu_7O_{15-\delta}$. T_c was determined by dc magnetic susceptibility measurements in a 0.9 mT magnetic field. The onset T_c values as obtained from the field-cooled experiment are given in Table I.

For the NQR and SEDOR experiments, we used unoriented powder samples, whereas the NMR experiment was done on a c-axis oriented powder sample.

All measurements were carried out by using standard pulsed spectrometers and the signal-to-noise ratio was improved by the phase alternating add-subtract spin-echo accumulation technique.

The NQR and SEDOR were done in zero external field.

TABLE I. T_c values of the nominal $YBa_{2-x}Ca_xCu_4O_8$ samples used in the experiments.

x	0	0.02	0.05	0.10
T_c (K)	81	82	88	91

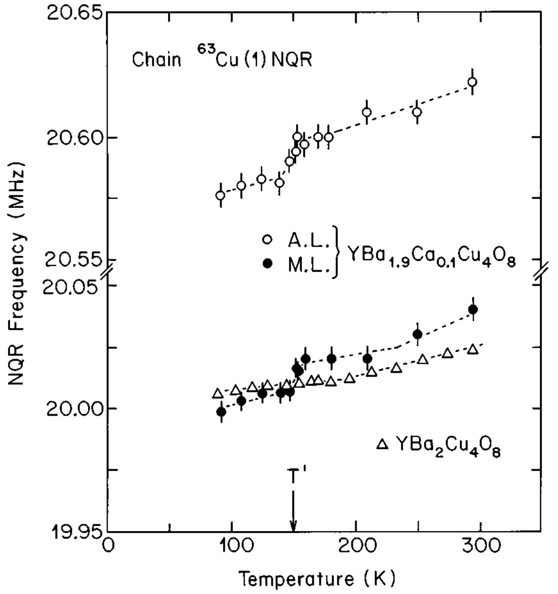

FIG. 1. Temperature dependence of chain ^{63}Cu(1) NQR frequencies in YBa$_2$Cu$_4$O$_8$ (△) and YBa$_{1.9}$Ca$_{0.1}$Cu$_4$O$_8$ (●, ML; ○, AL). ML and AL stand for *main* and *additional* line. In Ca-substituted YBa$_2$Cu$_4$O$_8$, a phase transition occurs at temperature T'.

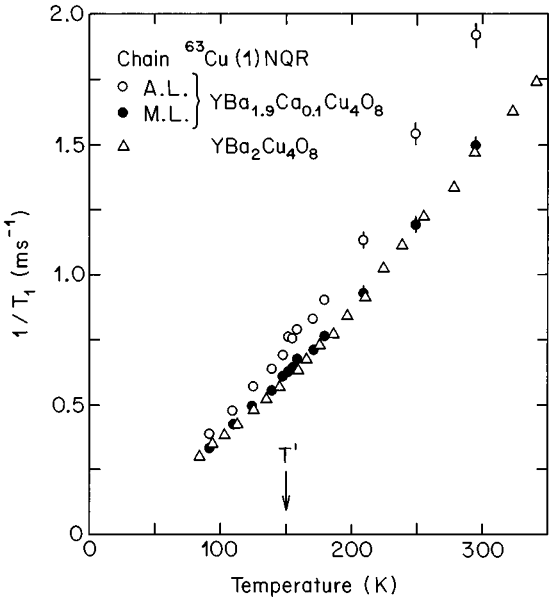

FIG. 2. Temperature dependence of chain ^{63}Cu(1) spin-lattice relaxation rate, $1/T_1$, in YBa$_2$Cu$_4$O$_8$ (△) and YBa$_{1.9}$Ca$_{0.1}$Cu$_4$O$_8$ (●, ML; ○, AL).

The spectra were obtained either by Fourier transformation of the spin echo or by scanning the frequency in discrete steps and integrating the spin-echo signal. The spin-lattice relaxation time, T_1, was determined by NQR using the inversion-recovery pulse sequence. The NMR was performed in an external magnetic field, B_0, of 9.03 T and the spectra were obtained by Fourier transformation of the spin echo.

In all our resonance experiments we used a slightly damped resonance circuit with a rather small coil (and consequently small samples) to achieve, if necessary, very short pulses and thus broad spectral excitation. To prevent sparking we kept the probe head in nitrogen gas at a pressure of 3 bars.

III. RESULTS AND DISCUSSION

A. Chain Cu NQR frequency and relaxation time

At first, we performed a set of measurements to provide convincing evidence, that the *additional* Cu line (AL), which appears about 600 kHz above the *main* chain Cu(1) line (ML) in Ca-substituted YBa$_2$Cu$_4$O$_8$,[3,12] does indeed stem from chain Cu sites disturbed by the "impurity" Ca ions. In Fig. 1 we present precise results for the temperature dependence of the AL and ML frequency from YBa$_{1.9}$Cu$_{0.1}$Cu$_4$O$_8$ in comparison with corresponding Cu(1) data obtained from pure YBa$_2$Cu$_4$O$_8$. Figure 2 shows the spin-lattice relaxation rate, $1/T_1$, measured on the same AL and ML compared again with $1/T_1$ of Cu(1) in pure YBa$_2$Cu$_4$O$_8$. Two issues concerning the AL and ML are obvious from the figures, namely, the following.

(i) The NQR frequencies, ν_Q, and relaxation rates of the two lines exhibit the same temperature dependence, however their values differ. ν_Q and $1/T_1$ of the ML are almost the same as the corresponding parameters of the chain Cu(1) line of pure YBa$_2$Cu$_4$O$_8$.

(ii) ν_Q and $1/T_1$ of both the ML and AL in YBa$_{1.9}$Ca$_{0.1}$Cu$_4$O$_8$ show distinctly an anomaly at 150 K not seen in pure YBa$_2$Cu$_4$O$_8$, that points out to the doping induced structural phase transition recently observed in specific heat,[8] elastic neutron scattering,[9] and x-ray diffraction[10] measurements.

From (i) and (ii) it is obvious that the ML and AL are intimately connected, and the AL cannot arise from "stacking faults" as proposed by Machi *et al.*[12]

B. Chain Cu spin-echo double resonance

To remove any doubts that the AL and ML come from Cu sites that are close neighbors we performed a spin-echo double resonance (SEDOR) experiment that involves simultaneously the AL Cu nuclear spins (I spins) and the ML Cu nuclear spins (S spins).

The SEDOR experiment proceeds as follows (see the inset in upper part of Fig. 3). We perform a spin-echo experiment on nuclear spin I, by applying an $\pi/2$-τ-π radio-frequency pulse sequence at the ν_Q of I and observing the echo of the I spins; τ denotes the time separation of the two pulses. In addition, we apply, at time τ_F after the $\pi/2$ pulse, another π pulse at the frequency of spin S. This pulse flips the S spin and thus changes the local field produced by S at I. Hence the echo formation of I is disturbed and consequently the echo reduced. The whole experiment works only if the spins I and S are coupled, meaning they have to be close neighbors. We have performed a similar experiment in Y$_2$Ba$_4$Cu$_7$O$_{15}$.[13]

We have employed two standard pulsed NQR spectrometers with appropriate modifications for the double-

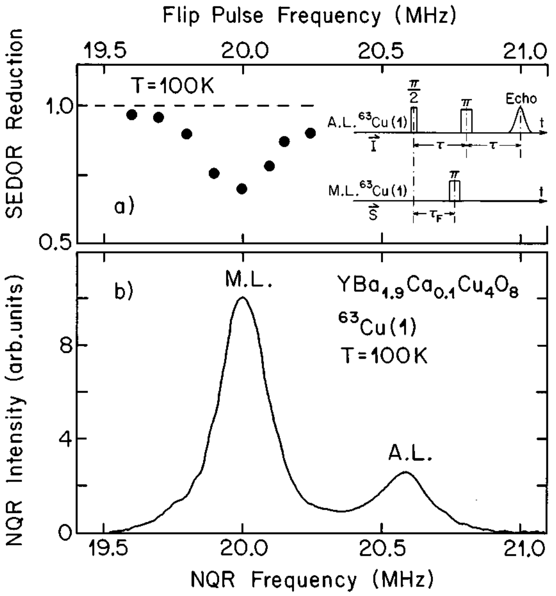

FIG. 3. SEDOR spectrum (a) and NQR spectrum (b) of chain ^{63}Cu(1) sites in YBa$_{1.9}$Ca$_{0.1}$Cu$_4$O$_8$ at 100 K. The spin echo of the ^{63}Cu(1) AL (I spin) is observed. The reduction of the spin echo is the strongest when the flip pulse frequency matches the ^{63}Cu(1) ML (S spin) frequency. The inset in (a) shows the used SEDOR pulse sequence.

resonance experiments. We have chosen the one-coil radio-frequency arrangement keeping τ and τ_F constant ($\tau = 300$ μs, $\tau_F = 290$ μs).[14,15]

Figure 3 presents the essential experimental result. The lower part shows the ^{63}Cu(1) NQR spectrum of YBa$_{1.9}$Ca$_{0.1}$Cu$_4$O$_8$ powder at 100 K with its main (ML) and additional line (AL). The upper part displays the reduction of the I (AL) spin-echo when the flip pulse is applied. The reduction is the strongest when the flip pulse frequency matches the spin S (ML) frequency. This positive SEDOR effect clearly demonstrates that the Cu spins of the AL and ML are coupled, presumably through direct dipolar coupling. Such a coupling is, of course, only possible if the sites delivering the AL and ML are close neighbors located, for instance, on the same double chain.

C. Intensity ratio of the additional and main chain Cu line

After we have firmly established that the AL arises from chain Cu(1) sites which are disturbed by the substituting Ca ions, we turn our attention to the intensity ratio R_I of the AL and ML. This ratio depends strongly on the lattice site the Ca ion occupies and on the origin and the extent of the disturbance. In order to proceed, we make the following assumptions concerning the origin of the different lines. The AL comes from those Cu(1) sites that are quadrupolarly disturbed nearest neighbors to a single Ca ion. The Cu(1) sites without a Ca ion as a nearest neighbor deliver the quasi-undisturbed ML, that behaves more or less as the Cu(1) line in pure YBa$_2$Cu$_4$O$_8$ (see Figs. 1 and 2). The leftover Cu(1) sites having two or more Ca ions as nearest neighbors, are on the other hand so much disturbed that their ν_Q lines get wiped out from the observed NQR spectrum. The number of different Cu(1) sites and thus the intensity of lines they form depends also on the distribution of Ca. We distinguish two possibilities: the Ca is either uniformly distributed without clustering or its distribution is completely random.

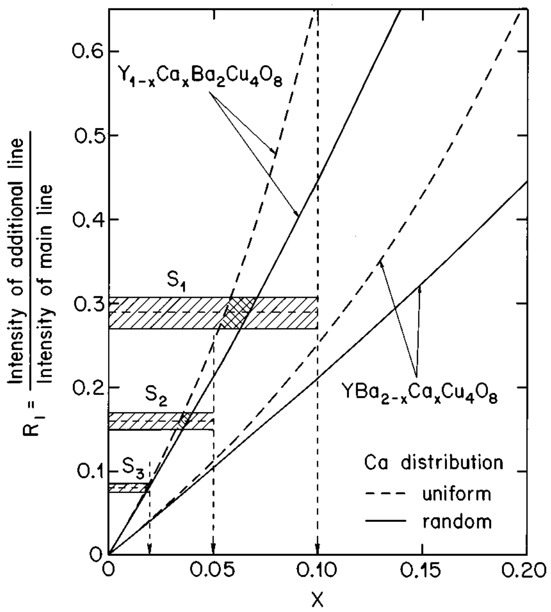

FIG. 4. Intensity ratio, R_I, of the additional and main Cu line vs the Ca concentration, x, per YBa$_2$Cu$_4$O$_8$ chemical formula unit. For the explanation of the different symbols see the text.

We will now discuss three cases of substitution:

(i) Ca^{2+} ions replace exclusively the higher-valent Y^{3+},

(ii) Ca^{2+} ions replace exclusively the isovalent Ba^{2+},

(iii) Ca^{2+} ions substitute partially Ba^{2+} and Y^{3+}.

Case (i). Each Ca ion has eight equivalent Cu(1) nearest neighbors. By simple counting the following expressions for R_I can be deduced: $R_I = 4x/(1-4x)$ for uniform and $R_I = 4x/(1-x)$ for random distribution, x denoting the Ca concentration per YBa$_2$Cu$_4$O$_8$ chemical formula unit. As expected, the two expressions yield practically the same R_I for small x.

Case (ii). The number of equivalent Cu(1) nearest neighbors around each Ca^{2+} reduces to four. Consequently, the previous R_I expressions change in that x is replaced by $x/2$.

Case (iii). The observed single AL comes from Cu(1) sites that are nearest neighbors either to Ca at Y site or to Ca at Ba site. We assume that whatever Ca does not contribute to the AL leaves Cu(1) undisturbed. The corresponding R_I is going to be somewhere between the values for cases (i) and (ii).

Figure 4 depicts R_I vs x for cases (i) and (ii), with a uniform and a random Ca distributions. The diagram includes for each sample S_i ($i = 1,2,3$) with nominal concentration $x_i = 0.10, 0.05, 0.02$, a horizontal hatched bar that represents the experimental ratio $R_{I,\mathrm{expt}}$ between the AL and ML intensity corrected by $\nu_Q^2(\mathrm{ML})/\nu_Q^2(\mathrm{AL}) = 0.94$. The thickness of the bar corresponds to the $R_{I,\mathrm{expt}}$ error limits whereas its length equals to the sample's x. As one can notice, all three bars do not touch the $R_I(x)$ curves calculated for YBa$_{2-x}$Ca$_x$Cu$_4$O$_8$ [case (ii)]. Within the scope of our assumptions, this eliminates the possibility that Ca^{2+} could

TABLE II. Parameters of the nominal $YBa_{2-x}Ca_xCu_4O_8$ samples used in the experiments.

Sample	S_1	S_2	S_3
x	0.10	0.05	0.02
x'	0.062(6)	0.035(3)	0.019(1)
$R_{I,\mathrm{expt}}$	0.29(2)	0.16(1)	0.081(5)

replace exclusively Ba^{2+}. On the other hand, the fact that S_3 touches the $R_I(x)$ curves calculated for $Y_{1-x}Ba_2Ca_xCu_4O_8$ [case (i)] tells us that for $x=0.02$ the AL has to arise from Cu(1) sites disturbed by Ca at Y site. The fact that S_2 and S_1 cross the $R_I(x)$ curves calculated for $Y_{1-x}Ba_2Ca_xCu_4O_8$ reveals that with increasing x, Ca does replace Y only partially. The corresponding partial amount, let us name it x', is represented through the doubly hatched area. In Table II we collect the relevant parameters of the different samples.

The R_I analysis shows that actually case (iii) applies, where the major part of Ca replaces Y and the rest presumably substitutes Ba. In accordance with this finding, the proper description of Ca-substituted $YBa_2Cu_4O_8$ should read $Y_{1-x'}Ca_{x'+y}Ba_{2-y}Cu_4O_8$ with $x'+y$ equal to x, the nominal Ca content. By this new description the chemical formula $YBa_{1.9}Ca_{0.1}Cu_4O_8$ of our $x=0.10$ sample having $x'=0.062$ should be corrected to $Y_{0.938}Ba_{1.962}Ca_{0.1}Cu_4O_8$. The evidence that at high doping levels Ca replaces also Ba besides Y has been found in recent extensive x-ray structure refinement investigations by Schwer *et al.*[16]

As an important result, it thus turned out that, at high Ca doping, the concentration of substituted Y sites, x', is appreciably smaller than the nominal x. Since it is x' which is responsible for a direct increase of the hole charge carrier concentration, n, one can understand why the increase of n and the effects connected with it, as for instance the planar Cu(2) spin-lattice relaxation rate[3,7] and the magnetic shift,[7] are so weakly dependent on x.

D. Planar Cu Knight shift

The planar Cu(2) Knight shift K_{spin} in Y-Ba-Cu-O is a sensitive indicator of n in the CuO_2 planes. With increasing n, K_{spin} increases as well as changes its temperature dependence. To check how Ca doping influences K_{spin} we measured the temperature dependence of the total magnetic shift K_{ab} of the c-axis oriented powder $x=0.10$ sample for the $c\perp B_0$ orientation. K_{ab} was determined from the ^{63}Cu(2) central line by the same fitting procedure as used in Refs. 17 and 18 taking into account, of course, the change of ν_Q and the linewidth through Ca doping.

The final results together with the corresponding K_{ab} data from $YBa_2Cu_3O_7$ (Ref. 19) and $YBa_2Cu_4O_8$ (Ref. 18) are presented in Fig. 5. As it is well known, K_{ab} consists of a temperature independent orbital and temperature dependent spin part (Knight shift) K_{spin}. Further, it is known from previous NMR studies that in the limits of error bars the orbital shifts of $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$ are the same, even though the n values in their CuO_2 planes are quite different. Having this in mind, we assume that the change of n by Ca substitution as well the substitution itself do not affect the orbital shift of Cu(2), which we therefore take the same in all three compounds.

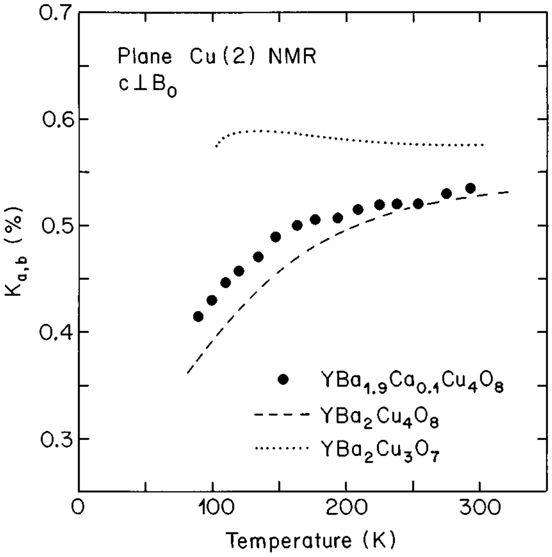

FIG. 5. Temperature dependence of the total magnetic shift, K_{ab}, of the planar Cu(2) in the c-axis oriented powder of $YBa_{1.9}Ca_{0.1}Cu_4O_8$ (●), $YBa_2Cu_4O_8$ (dashed line) from Ref. 18 and $YBa_2Cu_3O_7$ (dotted line) from Ref. 19, for the $c \perp B_0$ orientation.

Comparing now the three sets of shift data in Fig. 5 reveals that K_{ab} in $YBa_{1.9}Ca_{0.1}Cu_4O_8$, similar to K_{ab} in $YBa_2Cu_4O_8$, decreases with decreasing temperature, a signature that the compound is still underdoped, even though with a doping level somewhat higher than in $YBa_2Cu_4O_8$. From Fig. 5 it is also apparent that the doping level in $YBa_{1.9}Ca_{0.1}Cu_4O_8$ is definitely much lower than in $YBa_2Cu_3O_7$. This fact then raises the question: why do both compounds have almost the same T_c? It seems that, besides the increase of n, other effects have to play a role in the T_c enhancement. The minimal increase of n through Ca doping, as revealed by the shift data, is in qualitative agreement with the result from our R_I analysis.

E. Effect of Ca doping on ν_Q and T_1 of planar Cu

Since Ca^{2+}, as the R_I analysis has shown, predominantly occupies the Y site it should, due to the missing charge, strongly influence the electric field gradient (EFG) and hence ν_Q of the rather closely positioned Cu(2) in the nearby CuO_2 plane. The estimations based on a point charge model using for Cu an antishielding Sternheimer factor $(1-\gamma_\infty)\approx 20$ show, however, that due to geometrical reasons, ν_Q of the eight Cu(2), which are the nearest neighbors to the Ca^{2+} "impurity," *decreases* only by 0.4 MHz (the statement, in Ref. 3, that ν_Q increases in this case, is incorrect). For the 16 Cu(2) next nearest neighbors which are almost twice as distant from Ca^{2+} than the nearest ones, ν_Q decreases by 0.23 MHz, a value not much less than the previous 0.4 MHz.

The experimental ^{63,65}Cu(2) NQR lines in Ca-substituted $YBa_2Cu_4O_8$ exhibit two features, a bulge on the low-frequency side of the line that grows with x and a frequency shift of the peak of the line toward the higher frequencies.[3,12] For the $x=0.10$ compound, this frequency shift amounts to approximately 0.1 MHz with respect to Cu(2) ν_Q in pure $YBa_2Cu_4O_8$. The position of the bulge on the low frequency side of the line is in qualitative agreement with the estimated frequency decrease of Cu(2) that are nearest neighbors to the Ca^{2+} "impurity" at the Y^{3+} site.

It is an experimental fact that the planar Cu ν_Q in Y-Ba-Cu-O increases with growing n with a slope of approximately 23 MHz/hole/Cu.[17] To get the positive frequency shift due to the n increase in the $x=0.10$ sample we have to take into account also the estimated -0.23 MHz which the 16 next nearest Cu(2), that essentially deliver the bulk of the NQR line, experience directly from the "impurity" Ca^{2+}. The shift we are interested in is then equal to 0.33 MHz which corresponds to $\Delta n \approx 0.014$ hole/Cu(2) in the $x=0.10$ compound. This Δn compares well with the 0.015 hole/Cu(2) one gets in case the $x'=0.062(6)$ holes, introduced by the Y^{3+} substitution through Ca^{2+}, distribute equally over the two planes and the double chain.

As already apparent from K_{spin} results, also the change of Cu(2) ν_Q due to Ca substitution indicates only a modest increase of n for the optimal $x=0.10$ when T_c reaches its maximum. This once again supports the notion that besides the increase of n still other effects have to be involved in the observed T_c enhancement.

Finally, what is the effect of Ca substitution on Cu(2) T_1? It is well known for pure $YBa_2Cu_4O_8$ that $(T_1T)^{-1}$ reaches a maximum at a temperature T^* and that the drop of $(T_1T)^{-1}$ at lower temperatures is connected with the opening of a spin pseudo gap. At temperatures above T^*, $1/T_1$ of Cu(2) almost does not change by Ca substitution.[3,7] It could be that the partial substitution of Y by Ca, as demonstrated by K_{spin}, ν_Q and R_I, does not increase n sufficiently to be detected in $1/T_1$ Cu(2) above T^*.

Interesting, however, is that T^* definitely decreases with rising Ca content.[7] There are hints that the formation of the spin pseudo gap might be influenced by the interplane coupling in double-layer Y-Ba-Cu-O compounds.[22] One can imagine then that Ca at Y sites disturbs the interplane coupling and thus lowers T^*. If true this could offer an explanation for the unusually strong increase of T_c at rather modest increase of n. On the other hand, T^* is very close to T' so that a possible interdependence between them might exist. Further measurements, for instance on Y, could help to clear some of these open questions.

F. Phase transition at 150 K

As mentioned in the Introduction[8–10] and also seen in the temperature dependence of ν_Q and T_1 of both the AL and ML, a small but sharp change of various material parameters appears at $T' = 150$ K in Ca-substituted $YBa_2Cu_4O_8$ for $x \geqslant 0.025$. Since T' remains constant for x values in the range 0.025–0.10,[8] where T_c rises almost 10 K, it is questionable whether there is a link between the transition at T' and the superconducting properties. Most of the parameter anomalies at T' are indeed minute. For instance, the steplike relative decrease of ν_Q of both AL and ML is only about 0.06% (see Fig. 1). Similarly, the relative shrinking of the lattice parameters a and b amounts to no more than 0.025%.[9] This reduction of the lattice parameters can account for the observed drop of ν_Q at T', as can be easily estimated from the $1/r^3$ dependence of the EFG on the distance of an ionic point charge.

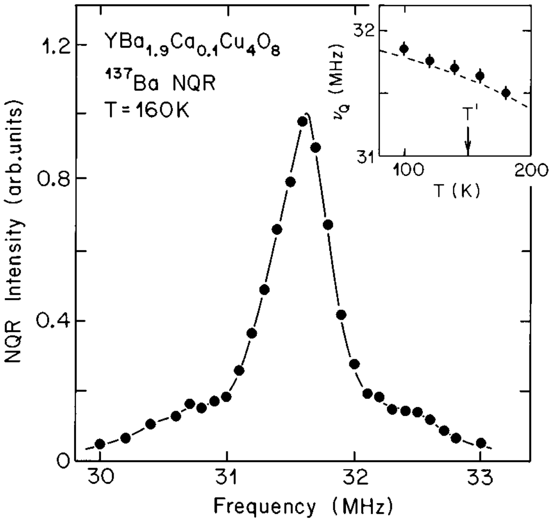

FIG. 6. ^{137}Ba NQR spectrum from $YBa_{1.9}Ca_{0.1}Cu_4O_8$ at 160 K. Inset: the temperature dependence of the ^{137}Ba line's peak in $YBa_{1.9}Ca_{0.1}Cu_4O_8$ (●) and $YBa_2Cu_4O_8$ (dashed line) from Ref. 21. The arrow shows the phase transition temperature T' in Ca-substituted $YBa_2Cu_4O_8$.

Less clear is another anomaly we discern at T', namely the ratio of the $1/T_1$ values of AL and ML. This ratio diminishes from the constant value 1.21(2) above T' to the constant value 1.14(1) below T'. The problem, to begin with, is that we do not understand why the AL relaxes faster than the ML. The Ca^{2+} "impurity" which is responsible for the AL formation, sits at the Y site and is thus quite distant from the chain Cu(1). It seems that the influence of the Ca^{2+} impurity onto Cu(1) is indirect and has to be mediated by the bridging apex oxygen which can easily effect the EFG and the magnetic hyperfine coupling of Cu(1). The later parameter is operative in the Cu(1) spin-lattice relaxation and may change at T'. This speculation gets support from a recent x-ray structural study[20] which reveals an anomaly in the bond length of the apex oxygen at T'.

To find out more about the transition at T' we wanted to see how it does affect the Ba ion. For this purpose we made some preliminary measurements looking at the temperature dependence of the NQR spectrum and T_1 of naturally abundant ^{137}Ba in the most studied $YBa_{1.9}Ca_{0.1}Cu_4O_8$ sample. The preliminary results are presented in Figs. 6 and 7.

The Ca doping broadens the ^{137}Ba NQR line which in addition gets a broad base with smeared structure (see Fig. 6). There is no well-separated additional line as in the Cu(1) case. The temperature dependence of the frequency of the ^{137}Ba line's peak can be seen in the inset of Fig. 6 (full circles) together with the data for pure $YBa_2Cu_4O_8$ (dashed line) from Ref. 21. There is hardly a difference between the two sets of data as well no anomaly appears at T'.

The same is valid for $1/T_1$ of the central part of the ^{137}Ba NQR line (Fig. 7). The corresponding data in pure

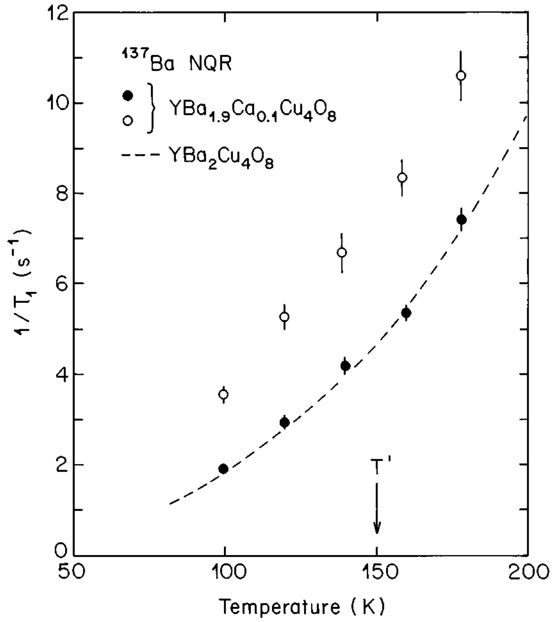

FIG. 7. Temperature dependence of the ^{137}Ba spin-lattice relaxation rate, $1/T_1$, of the central (●) and the base part (○) of the ^{137}Ba NQR line in $YBa_{1.9}Ca_{0.1}Cu_4O_8$ compared to ^{137}Ba $1/T_1$ in $YBa_2Cu_4O_8$ (dashed line) from Ref. 21.

$YBa_2Cu_4O_8$ are again taken from Ref. 21. We observe, however, that the base part of the ^{137}Ba line relaxes faster than the central part which is less disturbed by quadrupolar interactions. From Ba NQR studies in pure $YBa_2Cu_4O_8$ (Ref. 21) we know that the Ba spin-lattice relaxation is due to phonons and thus predominantly of quadrupolar origin. At the moment we do not know whether the additional relaxation the base part in $YBa_{1.9}Ca_{0.1}Cu_4O_8$ is experiencing, is of quadrupolar or magnetic origin. Measurements on the ^{135}Ba can clarify this question.

The inability to see any anomaly in $1/T_1$ and ν_Q of ^{137}Ba in $YBa_{1.9}Ca_{0.1}Cu_4O_8$, of course, does not necessarily mean that Ba does not experience the transition at T'. Probably, the anomaly is too small to be discerned in the less precise Ba NQR data.

IV. SUMMARY

By a set of NQR measurements including a SEDOR experiment, we provide convincing evidence that the additional Cu(1) line, AL, which appears about 600 kHz above the main chain Cu(1) line, ML, in Ca-substituted $YBa_2Cu_4O_8$,[3,12] does indeed stem from chain Cu sites disturbed by the "impurity" Ca ions. Through an analysis of the intensity ratio of the chain Cu AL and ML, R_I, we conclude that the "impurity" Ca ions, responsible for the AL, substitute Y^{3+}.

In addition, the R_I analysis has shown that at high Ca doping, the concentration of the substituted Y sites, x', is appreciably smaller than the nominal Ca concentration, x. Since it is x' which is responsible for a direct increase of the hole charge carrier concentration, n, one can on one hand understand why the increase of n and the effects connected with it, as for instance the planar Cu(2) spin lattice relaxation rate, ν_Q and the magnetic shift, are so weakly dependent on x.

On the other hand, the substantial increase of T_c with x suggests that, besides the increase of n, other effects have to play a role in the T_c enhancement. One of such effects might be the opening of the spin pseudo gap as revealed by the maximum of Cu(2) $(T_1T)^{-1}$ at temperature T^*. With rising Ca content, T^* definitely decreases.[7] There are hints that the formation of the spin pseudo gap might be influenced by the interplane coupling in double layer Y-Ba-Cu-O compounds.[22] Thus, one can imagine that Ca at Y sites, besides increasing n, could also disturb the interplane coupling and so lower T^* which in turn would boost the increase of T_c. This, of course, is only a speculation that needs to be more substantiated.

At T', ν_Q and $1/T_1$ of both the main and additional Cu(1) line in $YBa_{1.9}Ca_{0.1}Cu_4O_8$ show distinctly anomalies not seen in pure $YBa_2Cu_4O_8$, that point out the Ca doping induced structural phase transition recently observed in specific heat,[8] elastic neutron scattering, and x-ray diffraction[10] measurements. However, most of the anomalies observed at T' are indeed minute. Therefore, the inability to see them in $1/T_1$ and ν_Q of ^{137}Ba in $YBa_{1.9}Ca_{0.1}Cu_4O_8$ probably just lies in the insufficient precision of the collected ^{137}Ba NQR data.

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