Oxygen Isotope Effect of the Plane-Copper NQR Frequency in YBa$_2$Cu$_4$O$_8$

M. Mali, J. Roos, and H. Keller
Physik-Institut, Universität Zürich, CH–8057 Zürich, Switzerland

J. Karpinski
Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule Zürich, CH–8093 Zürich, Switzerland

K. Conder
Laboratory for Neutron Scattering, ETH Zürich and PSI Villigen, CH–5232 Villigen PSI, Switzerland

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We report on high-precision measurements of the temperature dependence of the plane$^{63}$Cu NQR line frequency $\nu_Q(Cu2)$ and the linewidth in normal and superconducting $^{18}$O and $^{18}$O exchanged YBa$_2$Cu$_4$O$_8$. Whereas $\nu_Q(Cu2)$ passes $T_c$ very smoothly without a discontinuity either in value nor in slope, the linewidth increases in the normal conducting phase down to $T_c$ and starts to decrease sharply in the superconducting phase to finally resume its high-temperature value of the normal phase.

There is a well discernible oxygen isotope effect on the $\nu_Q(Cu2)$ temperature dependencies. The temperature dependence of $\nu_Q(Cu2)$ is described by an empirical expression consisting of two parts: one related to the thermal expansion of the lattice and the other due to charge redistribution during the formation of new electronic structures in the CuO$_2$ planes. From the fit to the experimental data we determine for the conjectured formation of new electronic structures an energy scale $\Delta(16)$O = 188.0(1.6) K and $\Delta(18)$O = 180.0(1.6) K. This results in a partial oxygen isotope effect coefficient $\alpha_{\nu_Q} = 0.42(11)$ which is larger than both the spin-pseudogap coefficient $\alpha_{PG} = 0.061(8)$ and the $T_c$ coefficient $\alpha_{T_c} = 0.056(12)$.

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I. INTRODUCTION

In the past few years very strong experimental evidence has been found for static or dynamic charge inhomogeneities in strongly correlated electronic systems in particular in high-$T_c$ superconductors where an array of self organized one dimensional structures known as stripes can appear and with them the possibility of a pseudogap. Static charge redistributions might occur at the formation of new electronic structures. The nuclear quadrupole resonance (NQR) frequency ($\nu_Q$) being proportional to the electric field gradient (EFG) can serve as a very sensitive monitor of any such charge redistribution. The plane-copper (Cu2) nuclear quadrupole resonance frequency $\nu_Q(Cu2)$ in YBa$_2$Cu$_4$O$_8$ seems to signal such an event. Besides the effect of thermal lattice expansion, the temperature dependence of $\nu_Q(Cu2)$ reveals an additional effect possibly connected to the charge redistribution in the CuO$_2$ planes induced by some kind of a new electronic structure. The temperature dependence of $\nu_Q(Cu2)$ is very unconventional, particularly striking is the change of the course around 190 K where a broad minimum in the frequency appears. In the same temperature region other anomalies in nuclear magnetic resonance (NMR) and NQR quantities, for instance in Knight shifts, line widths, and relaxation times occur which signal an electronic crossover. To learn more about the CuO$_2$ planes especially about a possible charge redistribution during the pseudogap formation as well as to have very precise $\nu_Q(Cu2)$ values frequently demanded in other Cu2 NMR and NQR studies we decided to implement the Cu2 $\nu_Q$ and linewidth data by additional measurements on the very same material on which we recently determined by Cu2 spin-lattice relaxation the oxygen isotope effect of the spin-pseudogap. Therefore we performed between 5 K and 350 K very accurate measurements of the temperature dependence of the Cu2 NQR line frequency $\nu_Q(Cu2)$ and the linewidth in normal and superconducting $^{16}$O and $^{18}$O exchanged YBa$_2$Cu$_4$O$_8$. It is our anticipation that accurate knowledge of the influence of different oxygen isotopes onto $\nu_Q(Cu2)$ and its temperature dependence will add clues to the understanding of high-$T_c$ superconductors.

II. EXPERIMENTAL DETAILS

Sample preparation, oxygen exchange process and sample characterization are described in Ref. The $^{18}$O content in the $^{18}$O sample is 88% as determined by the weight loss of $^{18}$O material after back exchange of $^{18}$O with $^{16}$O. Room temperature x-ray measurements show a small difference in the lattice parameters of the two oxygen isotope samples. The $a$, $b$, and $c$ lattice parameters are 3.8411(1) Å, 3.8717(1) Å, 27.2372(8) Å for the $^{16}$O and 3.8408(1) Å, 3.8718(1) Å, 27.2366(8) Å for the $^{18}$O.

*Electronic address: mali@physik.unizh.ch
the $^{18}$O samples. For the detection of the NQR signal we used a standard NQR pulse spectrometer employing spin-echo technique and echo recording in quadrature. The magnitude of the complex Fourier transform of the whole echo delivered the shape and the position of the line. The two oxygen exchanged samples were inserted into a probe head with two identical resonance circuits which allowed simple switching of the electronics from one sample to the other thus minimizing the effects of any possible slow drifts in the characteristics of the equipment and temperature. To guarantee a proper excitation and detection of the relatively broad line we increased the damping of the resonance circuits by additional 7 Ω resistances. Further we used 6 mm diameter coils and highest power available (1 kW) such that a pulse of only 1.8 μs duration corresponded to a π pulse. We also took care to tune the resonance circuits as well as to excite the line with pulses at a frequency very close to the middle of the line, the difference between the two never exceeding more than 10 kHz. During the whole experiment we followed a rigid measurement procedure to ensure an equal treatment of the two samples.

III. ANALYSIS AND RESULTS

The shape of the Cu2 lines in both oxygen exchanged samples are identical and always asymmetric with a tail towards lower frequencies. To improve the reproducibility of the analysis we decided to take the center of gravity of the upper half of the line as the position of the line. The scatter of the line's position as defined above lies in the range of ± 2 kHz. Into the same range falls also the scatter of the linewidth defined as the full width at the half of the line’s maximum (FWHM). Figs. 1 and 2 exhibit the observed temperature dependence of the position and the linewidth of the Cu2 line in $^{16}$O and $^{18}$O YBa$_2$Cu$_4$O$_8$ samples. At first one clearly notices that the frequency data points of the $^{18}$O sample lie beneath the ones from the $^{16}$O sample and that the frequency shift of about 15 kHz between the two sets of data is roughly constant. A closer inspection, however, reveals that there is also a slight temperature shift between the two temperature dependences. This can be seen best at the temperatures where the frequencies have their minimum and the temperature dependences their largest slope. These temperatures lie lower for the $^{18}$O sample. Further one notices the extraordinarily smooth passage of the frequency from the normal to superconducting state. There is no jump in the frequency or even a slight change in its slope at $T_c$. Also unusual is the rather abrupt saturation of the temperature dependence of the frequency below 30 K. In contrast the linewidth of both $^{16}$O and $^{18}$O samples (Fig. 2) show within error no difference in the temperature dependence. The dependence itself is surprising and has not been observed in high-$T_c$ cuprates previously. Remarkable is the dramatic change of the course of the normal state linewidth temperature dependence at $T_c$ with the subsequent narrowing of the line in the superconducting state such that the line towards zero temperature resumes again its high temperature normal conducting state linewidth.

![Figure 1](image_url)  
FIG. 1: Temperature dependence of the NQR frequency of plane $^{63}$Cu2 in $^{18}$O (full triangles) and $^{16}$O (full circles) exchanged YBa$_2$Cu$_4$O$_8$. The solid lines are fits of Eq. (1) to the experimental data and the broken lines represent the conjectured temperature dependence of $\nu_Q$($^{63}$Cu2) that comes from the thermal expansion of the lattice.

IV. DISCUSSION

A. NQR frequency

With help of $\nu_Q$ one is able to monitor the electric field gradient (EFG) at the nuclear site of interest. The EFG, a ground state property of a solid, depends sensitively on the charge distribution in the solid. Thus knowledge of the EFG and its temperature dependence in a high-$T_c$ superconductor can contribute valuable information concerning the electronic properties of the material. The two naturally occurring copper isotopes $^{63}$Cu and $^{65}$Cu have nuclear spin 3/2 and quadrupole moments $^{63}Q$ and $^{65}Q$. In a EFG the Cu nuclei experience NQR at a single frequency $\nu_Q^{63,65} = (63,65QeV_{zz}/2\hbar) \cdot \sqrt{1 + \eta^2/3}$ where $V_{zz}$ is the major principal axes of the EFG tensor and $\eta$ the EFG asymmetry parameter defined as $\eta = (V_{xx} - V_{yy})/V_{zz}$. Here we used the convention: $|V_{xx}| < |V_{yy}| < |V_{zz}|$. To discuss the results a comparison with EFG calculations is necessary. The $ab\ initio$ calculations of the EFG are unfortunately not yet precise enough for a description of small changes of $\nu_Q$. 

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The Cu\textsubscript{2} atoms in the CuO\textsubscript{2} plane experience the EFG tensor at the Cu nucleus equivalent to about 70 MHz. The sign of \( \nu_{Q} \) experiences only the lattice part of the EFG which due to the thermal lattice expansion decreases with temperature. The authors of Ref. \[10\] could fit the temperature dependence of \( \nu_{Q}(\text{Ba}) \) quite accurately by a power law: 

\[
\nu_{Q}(T) = \nu_{Q}(0)(1 - AT^{1.43})
\]

In an effort to better discern the effect of the new electronic feature at low temperatures we attempt to extrapolate the normal high-temperature behaviour of \( \nu_{Q}(\text{Cu}2) \) to temperatures below 200 K. In doing so we assume that the power law used for \( \nu_{Q}(\text{Ba}) \) holds also for the lattice part of Cu2 EFG. After subtracting this extrapolation from the original \( \nu_{Q}(\text{Cu}2) \) data we get a "rest" whose temperature dependence looks very familiar, namely like the Cu2 Knight shift temperature dependence turned on head \[11\]. Lacking more insight we decide to fit this "rest" by an empirical function 

\[
B \tanh^2\left(\frac{\Delta}{2T}\right),
\]

where the constants \( A, B, C \) and \( \Delta \) are free fit parameters. The plus sign of the second term in the expression for \( \nu_{Q}(T) \) takes care of the fact that in case of Cu2, in contrast to Ba, the smaller lattice contribution to the EFG gets subtracted from the larger valence one. The obtained fit is quite good (see Fig. \[\text{FIG. 2}\]). The corresponding fit parameters are collected in the Table \[\text{I}\]. The difference in the quantum mechanical zero-point displacement and thermal lattice expansion can explain the nearly con-

\[
\nu_{Q}(T) = C + AT^{1.43} + B \tanh^2\left(\frac{\Delta}{2T}\right),
\]

with the constants \( A, B, C \) and \( \Delta \) as free fit parameters.

We use therefore a semi-empirical approach to the problem. We separate the EFG into two contributions: (i) the lattice part that refers to the charge distribution of the lattice ions surrounding the atom containing the nucleus in question and (ii) the valence contribution coming from electrons (holes) of the incompletely filled electronic shells of the same atom. The principal components of the EFG tensor \( V_{aa} \) add as: 

\[
V_{aa} = V_{\text{lattice}}^{\text{valence}} + V_{\text{valence}}^{\text{lattice}},
\]

where \( V_{\text{lattice}}^{\text{valence}} \) and \( V_{\text{valence}}^{\text{lattice}} \) denote the lattice and the valence part, respectively. Due to the point symmetry at the plane-copper (Cu2) site the principal axes of the EFG at this site lie along the crystallographic axes with the major principal axis \( V_{zz} \) parallel to the crystal c-axis \[\text{FIG. 1}\]. The Cu2 atoms in the CuO\textsubscript{2} plane act closely like Cu\textsuperscript{2+} ions with a hole in the \( x^2 - y^2 \) orbit. Bleaney and coworkers \[8\] show from electron spin resonance studies that a single hole in the d-shell gives rise to an axial EFG at the Cu nucleus equivalent to about 70 MHz. The sign of \( V_{\text{valence}}^{\text{valence}} \) from the hole in the \( x^2 - y^2 \) orbit is opposite to the sign of \( V_{\text{lattice}}^{\text{lattice}} \) produced mainly by the four negatively charged neighbour oxygen atoms. A rough estimate with the so-called point charge model, where the lattice ions are approximated by point charges, delivers \( V_{\text{valence}}^{\text{lattice}} \) half the size of \( V_{\text{valence}}^{\text{valence}} \). Therefore in case of Cu2 the sum of the two EFG parts of opposite sign turns out to be a difference governed by the larger valence part. The valence contribution to the EFG remains temperature independent (the valence does not change) whereas the lattice part diminishes with increasing temperature due to the thermal expansion of the lattice. Applied to Cu2 this would mean an increase of the summed EFG and thus an increase of \( \nu_{Q} \) with increasing temperature. Such a behavior is indeed observed for Cu2 in YBa\textsubscript{2}Cu\textsubscript{4}O\textsubscript{8}, but only for temperatures above 200 K. Below 200 K the behavior changes completely so that towards lower temperatures \( \nu_{Q} \) instead decreasing starts to grow and finally saturates at 30 K. Since a high resolution neutron powder diffraction study \[9\] shows that the crystal axes of YBa\textsubscript{2}Cu\textsubscript{4}O\textsubscript{8} increase smoothly with temperature a change of the \( \nu_{Q} \) temperature behavior at 200 K signals something new, a feature that most likely is connected to the electronic system of the CuO\textsubscript{2} planes. That the lattice of YBa\textsubscript{2}Cu\textsubscript{4}O\textsubscript{8s} indeed behaves in a conventional way one can also learn from the temperature dependence of \( \nu_{Q}(\text{Ba}) \), which smoothly decreases with temperature from the lowest (5 K) to the highest (400 K) temperatures \[10\]. The Ba ion has a filled electron shell and therefore experiences only the lattice part of the EFG which due to the thermal lattice expansion decreases with temperature.

FIG. 2: Temperature dependence of the linewidth of the plane \( ^{63}\text{Cu}2 \) NQR line in \( ^{16}\text{O} \) and \( ^{18}\text{O} \) exchanged YBa\textsubscript{2}Cu\textsubscript{4}O\textsubscript{8}. The solid line is a fit of Eq. \[2\] to the linewidth data in the normal conducting state.

| \( \Delta \) (K) | \( A \) (MHzK\textsuperscript{−1.43}) | \( B \) (MHz) | \( C \) (MHz) |
|-----------------|-----------------|-----------------|-----------------|
| \( ^{16}\text{O} \) 188.0(1.6) | 2.59(7) \times 10^{-3} | 0.184(2) | 29.642(3) |
| \( ^{18}\text{O} \) 180.0(1.6) | 2.69(6) \times 10^{-5} | 0.182(2) | 29.629(2) |
stant 15 kHz shift in the lattice part of the EFG between the $^{16}\text{O}$ and $^{18}\text{O}$ samples. The heavier $^{18}\text{O}$ has a smaller zero-point and thermal fluctuation amplitude than $^{16}\text{O}$ and therefore expands the lattice less than $^{16}\text{O}$ as observed by the x-ray measurement of the lattice parameters. Consequently the lattice part of the EFG in the $^{18}\text{O}$ sample is larger than in the $^{16}\text{O}$ sample which leads in case of Cu2 to a lower $\nu_Q$. Of greater interest is the parameter $\Delta$ representing the energy scale of the $\nu_Q$ feature. Its value though close to the magnitude of the spin-pseudogap is definitely smaller than the later one. Further, the oxygen isotope effect on $\Delta$ is substantial. The corresponding partial oxygen isotope effect coefficient is $\alpha_{\nu Q} = 0.42(11)$ and thus much larger than both the spin-pseudogap coefficient $\alpha_{PG} = 0.061(8)$ and the $T_c$ coefficient $\alpha_{T_c} = 0.056(12)$.[5] The EFG does not depend on spin but exclusively on charge, however, on all charges, irrespective what state they occupy. In that respect the EFG differs from the Knight shift and spin-lattice relaxation which experience only the spins of the charge carriers whose energies are close to the Fermi level. Therefore, in case of the EFG, at the formation of a pseudogap all the electrons have to be considered, not just those close to Fermi surface. This makes conclusions on the basis of an empirical analysis as ours rather uncertain. Nevertheless, the observed large oxygen isotope effect on the temperature dependence of $\nu_Q$(Cu2) indicates that the involved charge feature in the CuO$_2$ planes is influenced by the coupling of the charge carriers to the lattice as it is the case for spin-pseudogap and superconductivity.

B. Linewidth

The linewidths of the Cu2 NQR lines from the two oxygen isotope samples (Fig. 3) are equal within error at all temperatures. Further, we find that at 350 K the linewidth ratio of the $^{63}\text{Cu}$ and $^{65}\text{Cu}$ isotope NQR lines is 1.085(7) which within error equals to the ratio (1.0806) of the isotopes’ nuclear quadrupole moments. This allows the conclusion that at 350 K the line is broadened predominantly by quadrupolar effects produced by static EFG inhomogeneities in the material. Such inhomogeneities, in principle, could be of intrinsic origin generated for instance by a charge instability in the electronic system of the plane. However, this possibility most probably can be excluded since a comparison of linewidths measured at 350 K in YBa$_2$Cu$_4$O$_8$ samples from different batches, shows a variation of these quadrupolar linewidths depending on the parameters of material preparation. Since the superconducting properties are not sensitive to the structural disorder there is not much incentive to invest for NQR purpose alone into the time consuming improvement of the preparation parameters necessary to make a structurally perfect material. Nevertheless, the obtained $^{63}\text{Cu}$Cu2 line with its 125 kHz linewidth at room temperature is to our knowledge the narrowest plane $^{63}\text{Cu}$ NQR line yet observed in high-$T_c$ cuprates. Though this proves the high quality of our samples improvements certainly are still possible, especially for a stoichiometric material as YBa$_2$Cu$_3$O$_8$ where one expects an order of magnitude narrower lines. The observed lines are broadened asymmetric having a tail towards lower frequencies. Comparison with the Ba NQR line suggests that this asymmetry has to come from a lattice imperfection that produces simultaneously an EFG inhomogeneity at Cu2 and Ba sites since the shape of Ba NQR line is asymmetric too but with a tail towards higher frequencies. Lattice defects can produce various EFG inhomogeneities. The defect we observe, is somewhat special since it can produce opposite line asymmetries for Cu2 and Ba NQR lines. A possible candidate that could do so would be for instance a lattice defect that locally shrinks the lattice and thus increases the lattice part of EFG at both Cu2 and Ba sites. As already mentioned, any increase of lattice EFG pushes Ba and Cu2 NQR frequencies in opposite direction, it increases the Ba and decreases the Cu2 one what explains the opposite lineshape asymmetries. The asymmetry of the lines does not change with temperature. Even though asymmetric, the Cu2 line is narrow enough to allow a very precise measurement of the broadening of the line with decreasing temperature in the normal conducting state and what is more important it enables in a high $T_c$-cuprate to discern how a plane-Cu line gets narrow again below $T_c$. The observed change in the temperature behaviour at $T_c$ is extremely sharp with a very rapid decrease of the linewidth at the passage into the superconducting state where the line continues to narrow at approach to zero temperature its smallest normal state high temperature value. This behaviour, most likely intrinsic in YBa$_2$Cu$_4$O$_8$, has not been observed yet in other high-$T_c$ cuprates. It is the excessively broad plane-Cu lines in other cuprates that do not allow a similar observation. Most of cuprates are plagued by structural disorder generated by the only possible nonstoichiometric doping alternative. In YBa$_2$Cu$_4$O$_8$ at temperatures just above $T_c$ where the Cu2 line is broadest the ratio of the linewidths of the $^{63}\text{Cu}$ and $^{65}\text{Cu}$ isotopes decreases from the high temperature value to 1.06(1) which is smaller than the ratio of the two isotopes’ quadrupole moment and thus signals very likely a magnetic component in the line broadening. In case of pure magnetic broadening of the line the ratio of the linewidths of the two isotopes would be equal to the quotient of the corresponding Cu isotope gyromagnetic ratios $^{63}\gamma/^{65}\gamma = 0.9335$. That a magnetic broadening of the line with decreasing temperature indeed takes place we can also infer from the temperature dependence of the indirect Gaussian contribution $1/T_{2G}^\text{ind}$ to the Cu2 spin-spin relaxation rate [12] that comes from the nuclear magnetization transfer via the itinerant electron spin system and which is proportional to the static electron spin susceptibility $(\chi(Q_{AF}, \omega = 0))$ at the antiferromagnetic wave vector $Q_{AF}$. With decreasing temperature $\chi(Q_{AF}, \omega = 0)$ exhibits a Curie like behaviour
Its contribution to spin-spin relaxation is Curie like and presumably the same is true for the linewidth. To find out the temperature dependent contribution to the linewidth we try to deconvolute the total linewidth into its temperature independent and dependent parts. We find the linewidth at the lowest temperatures to be equal to the linewidth at the highest temperature where the magnetic contribution due to the Curie like behavior of $\chi(Q_{AF}, \omega = 0)$ is expected to be rather small and the only remaining contribution is then quadrupolar as we already noticed before. Usually a quadrupolar contribution that comes from lattice imperfections and has the observed large size does not vary much with temperature. Since we find the linewidths at the two temperature extrema equal we assume that we have an ”underground” quadrupolar contribution that remains constant throughout the whole temperature range. In general the broadening of a line caused by a combined operation of two distinct mechanisms is rather complex. There are few cases where simple relations exist as for instance for two Lorentzian or two Gaussian like line broadenings where in the first case the contributions add linearly and in the second quadratically. We do not expect that the broadening of a line caused by a combined operation of two quadrupolar contribution that remains constant through out the whole temperature range. For this purpose we fit the data gained in the normal conducting state so that we keep the underground quadrupolar part of the linewidth constant and allow the temperature dependent part to vary Curie like with temperature. For the fit procedure we use the following expression:

$$ (\delta \nu_{tot}(T))^n = (\delta \nu_{quad})^n + (C/T)^n. \quad (2) $$

The fit of the normal conducting state data yields: $\delta \nu_{quad} = 124(1)$ kHz, $C = 3.0(4)$ MHzK, and power $n = 1.24(7)$. With help of the parameters $\delta \nu_{quad}$ and $n$ we afterwards decompose the measured linewidth data to get the wanted temperature dependent contribution to the linewidth, $\delta \nu(T)$. The final result is presented in Fig. 3. As one can see the temperature dependent part of the linewidth tends to a value close to zero when the temperature approaches zero. The temperature dependent part of the linewidth can be of magnetic and of quadrupolar origin. Due to the large static electronic susceptibility at $Q_{AF}$ the magnetic part of the linewidth comes predominantly from the staggered magnetization induced by intrinsic as well as extrinsic magnetic field components at $Q_{AF}$. From $1/T_{2\Omega}^{2\Omega}$ measurements in the superconducting state $^{12}$ we know that $\chi(Q_{AF}, \omega = 0)$ decreases only 15% of its value at $T_c$ when going far into the superconducting state. Therefore, the reduction of the magnetic part of the NQR linewidth in the superconducting state has to come from a reduction or screening of the extrinsic magnetic fields in the superconducting state. From our measurements it is obvious that with decreasing temperature the NQR line broaden smoothly as long as the sample stays normal conducting but starts sharply to narrow when the sample turns superconducting. The whole increase in linewidth accumulated from 350 K down to $T_c$ disappears away in the superconducting state. At the moment we do not have an adequate explanation of this very unusual behavior of the linewidth of the Cu2 NQR line below $T_c$.

![Diagram](image.jpg)

**FIG. 3:** The temperature dependent contribution to the linewidth of the plane $^{63}$Cu2 NQR line in $^{16}$O and $^{18}$O exchanged YBa2Cu4O8.

**V. SUMMARY**

We performed accurate measurements of the temperature dependence of the $^{63}$Cu2 NQR line frequency and linewidth in normal and superconducting $^{16}$O and $^{18}$O exchanged YBa2Cu4O8. At the transition of YBa2Cu4O8 from normal into the superconducting phase we observe that $\nu_Q(Cu2)$ passes $T_c$ very smoothly without a discontinuity either in value nor in slope. In contrast to $\nu_Q(Cu2)$, the linewidth exhibits a drastic change of the course at $T_c$. While increasing in the normal conducting phase down to $T_c$, the linewidth starts to decrease sharply in the superconducting phase to finally resume towards zero temperature its high-temperature value in the normal conducting phase. Such a behavior of the narrow plane-copper NQR line in YBa2Cu4O8 has not been observed yet in other high-$T_c$ cuprates. At the moment we do not have an adequate explanation of this extraordinary temperature dependence of the Cu2 linewidth. The frequency
\( \nu_Q(\text{Cu2}) \) of \( ^{18}\text{O} \) exchanged YBa\(_2\)Cu\(_4\)O\(_8\) is always lower than \( \nu_Q(\text{Cu2}) \) of \( ^{16}\text{O} \) exchanged YBa\(_2\)Cu\(_4\)O\(_8\). The nearly constant frequency shift of 15 kHz can be accounted for by the difference in the quantum mechanical zero-point displacement and thermal lattice expansion between the \( ^{16}\text{O} \) and \( ^{18}\text{O} \) samples. More important, there is a well discernible temperature shift between the \( \nu_Q(\text{Cu2}) \) temperature dependencies of the \( ^{16}\text{O} \) and \( ^{18}\text{O} \) samples. Lacking a detailed theoretical description we attempt empirically to decompose the temperature dependence of \( \nu_Q(\text{Cu2}) \) into two parts: one part coming from the thermal expansion of the lattice and the other produced by the charge redistribution during the formation of new electronic structures in the CuO\(_2\) planes. From the fit of the empirical expression for \( \nu_Q(T) \) to the experimental data we determine for the conjectured formation of new electronic structures an energy scale \( \Delta = 188.0(1.6) \text{ K} \) for the \( ^{16}\text{O} \) and 180.0(1.6) K for the \( ^{18}\text{O} \) exchanged YBa\(_2\)Cu\(_4\)O\(_8\). The corresponding partial oxygen isotope effect coefficient \( \alpha_{\nu_Q} = 0.42(11) \) is much larger than both the spin-pseudogap coefficient \( \alpha_{PG} = 0.061(8) \) and the \( T_c \) coefficient \( \alpha_{T_c} = 0.056(12) \). [1]

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[1] F. Raffa, T. Ohno, M. Mali, J. Roos, D. Brinkmann, K. Conder, and M. Eremin, Phys. Rev. Lett. 81, 5912 (1998).
[2] V.J. Emery, S.A. Kivelson, and J.M. Tranquada, Proc. Natl. Acad. Sci. USA 96, 8814 (1999).
[3] H. Zimmermann, M. Mali, D. Brinkmann, J. Karpinski, E. Kaldis, and S. Rusiecki, Physica C 159, 681 (1989).
[4] A. Suter, M. Mali, J. Roos, D. Brinkmann, J. Karpinski, and E. Kaldis, Phys. Rev. B 56, 5542 (1997).
[5] A. Suter, M. Mali, J. Roos, and D. Brinkmann, Phys. Rev. Lett. 21, 4938 (2000).
[6] K. Schwarz, C. Ambrosch-Draxl, and P. Blaha, Phys. Rev. B 44, 5141 (1991).
[7] P. Hüsler, H.U. Suter, E.P. Stoll, and P.F. Meier, Phys. Rev. B 62, 1567 (2000).
[8] A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of transition Ions (Oxford University Press, New York, 1980).
[9] E. Kaldis, P. Fischer, A.W. Hewat, E.A. Hewat, J. Karpinski, and S. Rusiecki, Physica C 159, 668 (1989).
[10] A. Lombardi, M. Mali, J. Roos, and D. Brinkmann, Physica C 267, 261 (1996).
[11] M. Bankay, M. Mali, J. Roos, and D. Brinkmann, Phys. Rev. B 50, 6416 (1994).
[12] R. Stern, M. Mali, J. Roos, and D. Brinkmann, Phys. Rev. B 51, 15478 (1995).