Possible Relationship between Cu-NQR Frequencies and Cu Valence States in CuO\(_2\)-Planes for High-\(T_c\) Superconductors

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Abstract. We report on \(^{63}\text{Cu}\)-NQR frequency \(\nu\) measurements on various high-\(T_c\) superconductors. An empirical relationship between \(T_c\) and \(v\) is presented. We attribute this finding to variations in the valence state of the in-plane Cu ions which, due to the unusual electric polarizability of the \(\text{O}^{2-}\) ions, depends sensitively on the Cu–O distance.

1. Introduction

There is general agreement that in the actually known high-\(T_c\) cuprates the CuO\(_2\)-planes are the essential structural element to enable \(T_c\) values of about 100 K. Although the number of CuO\(_2\)-planes may successfully be used to make plausible the high \(T_c\) values in the series of multi-layered Tl- and Bi-based superconductors, it is not sufficient to explain the difference in the transition temperature of different cuprates containing the same number of CuO\(_2\)-layers. Therefore, based on semi-empirical approaches and on experimentally found variations in the in-plane Cu–O bond-length or covalency, various attempts have been made [1–4] in order to clarify the relationship between the structural properties and \(T_c\) of the high-\(T_c\) compounds.

Whangbo et al. [1], who examined the correlation between \(T_c\) and the in-plane Cu–O bond-lengths \(r_{\text{Cu–O}}\) for the Tl- and Bi-containing copper-oxide superconductors as well as for La\(_{2-x}\)Sr\(_x\)CuO\(_y\), group the experimental \(T_c\) vs. the \(r_{\text{Cu–O}}\) data into three major classes characterized by the sizes of the cations La\(^{3+}\), Ba\(^{2+}\), or Sr\(^{2+}\) occupying the 9-coordination sites connected with the apical oxygen ions. In each class they observe an optimum in-plane Cu–O distance \(r_{\text{opt}}\) for which \(T_c\) becomes a maximum. In this context it is interesting to mention that, considering only the optimum Cu–O distance,
we find moreover a clear tendency of increasing $T_{c_{\text{max}}}$ with increasing $r_{\text{Cu-O}}^{\text{opt}}$.

On the other hand, de Leeuw et al. [2] calculated the formal valence of the copper and oxygen ions in the central CuO$_2$-layer by using the Cu-O bond-length and applying Zachariasen rules. They found for a number of high-$T_c$ compounds that the maximum transition temperature, $T_{c_{\text{max}}}$, increases with decreasing "bond valence sum" of the in-plane copper ions. To explain this correlation they suggested that a higher $T_{c_{\text{max}}}$ is obtained if the holes in the CuO$_2$-planes prefer the oxygen sites over the Cu sites, which can equally be expressed in terms of the formal Cu(2) valence. Accordingly, a valence state of in-plane copper ions close to 3+ is rather unfavorable for superconductivity.

We would like to emphasize that the correlation between the hole density and $r_{\text{Cu-O}}$ cannot be calculated adequately within the framework of tight-binding band electronic structure calculations, because the unusual $r_{\text{Cu-O}}$ dependence of the electric polarizability [5,6] of the O$^{2-}$ ions plays an important role in oxides [5,6] and therefore cannot be neglected. Hence an experimental method, such as nuclear quadrupole resonance (NQR), which allows to gain more insight into the role of varying Cu-O bond-lengths and valence states of both the copper and the oxygen ions in cuprate superconductors, is of particular interest. The nuclear quadrupole resonance frequency $\nu_{\text{NQR}}$ of a copper nucleus is directly proportional to the electric field gradient $q_{zz}$ at the nuclear site. Its origin is the non-spherical (non-cubic) source-charge distribution around the respective Cu nucleus and therefore $q_{zz}$ is very sensitive to any change of the electronic configuration (the formal valence) of both the Cu and oxygen ions in these compounds.

### 2. Experimental

The NQR measurements were performed with a conventional home-built NMR pulse spectrometer in the temperature range of 4.2 K up to room temperature. The NQR spectra, which are presented in Fig.1, were obtained in the following way. A $\pi/2-\tau-\pi$ pulse-sequence with pulse-widths of respectively 5 µs and 10 µs, and a separation time of $\tau = 30$ µs, was applied for a set of selected frequencies. For each of these frequencies (at retuned resonance circuit) the spin-echo signal was measured in quadrature detection and, after Fourier transformation, the magnitude of the Fourier component at the respective excitation frequency was taken as the NQR amplitude at this frequency. Thus, by combining these data for the whole set of excitation frequencies, the full NQR spectrum was obtained. (A possible frequency dependence of the spectrometer, however, was not taken into account.) We mention that this time consuming procedure had to be applied since the