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Comment on "Localized behavior near the Zn impurity in $YBa_2Cu_4O_8$ as measured by nuclear quadrupole resonance"

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Williams and Krämer [Phys. Rev. B **64**, 104506 (2001)] have recently argued against the existence of staggered magnetic moments residing on several lattice sites around Zn impurities in $YBa_2Cu_4O_8$ superconductors. This claim, which is in line with an earlier publication by Williams, Tallon, and Dupree [Phys. Rev. B, **61**, 4319 (2000)], is, however, in contradiction with a large body of experimental data from different nuclear magnetic resonance (NMR) groups. On the contrary, the authors argue in favor of a very localized spin and charge density on Cu sites that are first neighbors to Zn. We show that the conclusions of Williams and Krämer arise from erroneous interpretations of NMR and nuclear quadrupole resonance data.

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I. INTRODUCTION

In a recent paper,[1] Williams and Krämer (hereafter WK) report on the nuclear quadrupole resonance (NQR) study of a new Cu line in the Zn-doped high-T_c superconductor (HTSC) $YBa_2Cu_4O_8$. This line was discovered by Williams *et al.*[2] and was confirmed by Itoh *et al.*,[3,4] while it is also possibly visible in an earlier report by Yamagata *et al.*[5] WK argue that this resonance arises from the four Cu first neighbors (Cu_{NN}) of each Zn impurity in CuO_2 planes. To our knowledge, this is the first time that this very special site can be resolved through a well-defined line in a Cu NQR spectrum. This isolated Cu resonance might thus be (somehow) equivalent to the ^{89}Y nuclear magnetic resonance (NMR) satellite discovered by Mahajan *et al.* in 1994.[6,7] The work of WK is potentially important because the immediate vicinity of Zn is crucial for understanding impurities in cuprates. For example, while the presence of staggered magnetic moments around impurities has been widely established,[8–12] the moment on Cu_{NN} has sometimes been described as a local moment giving rise to the surrounding staggered response,[6,9] while others have considered Cu_{NN} simply as the first site where the staggered response appears, in reaction to the broken translational symmetry of AF couplings.[10] The two descriptions are probably indistinguishable from an experimental point of view, as they both support a very large moment on Cu_{NN} and an extended staggered polarization with some decay as a function of distance from the impurity. Despite these differences in the descriptions, it is important to note that there is no disagreement between various linewidth data sets from the different NMR groups.

Nevertheless, Williams and Krämer argue in favor of a very localized spin and charge density on Cu sites which are first neighbors of Zn atoms, and against the existence of the staggered magnetic moments.[1] These statements, following earlier claims by Williams *et al.*,[2] are in contradiction with the facts established by the rest of the NMR community.[8–12] We show here that the conclusions of WK cannot be sustained by their NQR measurements. Other comments on the work of WK, complementary to those presented here, can be found in the comprehensive study of Itoh *et al.*[4]

II. NQR SPECTROSCOPY

Williams and Krämer state that the observation of a resolved line implies that there is "very localized charge and spin on the Cu sites that are nearest neighbor to the Zn impurity." We disagree with this view.

First, it is not possible to address the problem of the spin density here: because NQR is performed in zero external magnetic field, there is no measurable staggered magnetization, thus no NQR line broadening (unless magnetic moments are partially frozen on the time scale of the experiment, which is not the case in the temperature range investigated in Ref. 1).

Second, the conclusion of WK regarding the charge density is based on the assumption that "for small changes the difference between the ^{63}Cu NQR frequency at the Cu_{NN} and Cu_{NNN} sites is proportional to the change in the hole concentration." This assumption is quite questionable. While the ^{63}Cu NQR frequency $^{63}\nu_{NQR}$ can indeed be related to the average on-site hole density,[13,14] this does not mean that the "lattice" contribution (charge from surrounding sites[15]) is negligible. As an experimental counterexample, Zn-doping in undoped La_2CuO_4 induces modifications of the Cu NQR frequency,[16] which are comparable to the 4% relative change observed here by Williams and Krämer.[1] Because there are no doped holes in La_2CuO_4, the effect must come from a "lattice" contribution. The substitution of a Cu atom by Zn is expected to modify the electric field gradient tensor at the Cu_{NN} site, as both the lattice contribution and the local symmetry change. Hence, there is no *a priori* reason for the Cu_{NN} site to have almost the same NQR frequency as the sites far from the impurity. For example, recent state-of-the-art calculations of electric field gradients by Bersier *et al.* show that the change in $^{63}\nu_{NQR}$ is readily explained by a small shift of the O_{NN} position.[17]

III. ^{63}Cu NQR T_1

In Zn-doped YBCO, the spin-lattice relaxation rate of ^{63}Cu nuclei ($1/^{63}T_1$) does not show the characteristic drop observed below 150 K in pure samples (pseudogap behavior), but continues to increase with decreasing T.[1,3,10,18] WK correctly point out that this increase does not *necessarily* imply an enhancement of AF correlations. However, inelastic neutron scattering measurements have demonstrated that the enhancement occurs only for q close to the AF wave vector $(\pi/a,\pi/a)$ and only for energies ω below the pseudogap energy scale.[19] This means that Zn doping does enhance AF fluctuations at low energy. In this context, the expression "enhanced AF correlations" (introduced for spin chains[20]) simply means "enhanced staggered magnetization," which is the zero-frequency limit of the AF spin fluctuations.

According to WK, it is "unlikely that the $1/{}^{63}T_1T$ data can be interpreted within the enhanced antiferromagnetic correlation model $[\cdots]$. Rather, $1/{}^{63}T_1T$ at low T in substituted samples just appears to be a continuation of the Curie-like behavior observed in the pure materials for high temperatures." To our knowledge, there is no theoretical argument according to which the dynamics of the staggered moments[20] is incompatible with a Curie-like behavior for $1/{}^{63}T_1T$, should this behavior already be present at high T or not. Actually, in the context of the cuprates, the Curie-Weiss behavior is even suggestive of AF correlations: it is precisely in this way that the high-T behavior of ${}^{63}T_1$ has been interpreted by the entire NMR community to date. A smooth evolution from the pure to the Zn-doped materials would thus not be surprising, as there is no difference in the bare electronic *structure* between sites where the magnetization is enhanced and those where it is reduced: One always deals with the same correlated Cu^{2+} moments and the bare AF coupling remains the same, only the on-site magnetization changes smoothly as a function of position in the plane and as a function of T. We also note that for a magnetic correlation length of two to three lattice spacings, a sizeable magnetization exists on most sites for Zn-doping values of only a few percent. Thus it is probably inappropriate to think in terms of separate dynamics for the first neighbors of each impurity and for the "bulk" (although some spatial inhomogeneity in the spin dynamics probably exists even within this purely magnetic picture[21]).

IV. ^{63}Cu NQR T_2

Williams and Krämer find that, for Cu sites which are *not* nearest neighbors to Zn, ${}^{63}T_{2G}$ is close to the value obtained in the pure compound. They infer that the spins remain "like," and they conclude that "this provides further evidence, within the MMP model, that there is no suppression or enhancement of AF correlations for distances greater than one lattice parameter away from the Zn impurity."

We disagree with this, for several reasons. First, it must be emphasized that it has always been believed in cuprates that "like" spins do not contribute to spin-spin relaxation, and formulas that are used for the interpretation of T_{2G} take into account only the $I_z^iI_z^j$ terms and not the $I_+^iI_-^j$ ones.[22] Therefore, any distribution of local magnetization should not affect T_{2G} directly. Second, the NQR line, at variance with the NMR one, is not broadened by the staggered magnetization around the Zn ions, because in zero external field no static local field (on the NQR time scale) is induced. Thus the arguments of Williams and Krämer would not apply to their own data. Finally, as already stated above, the expression "enhanced AF correlations" has been used for an enhancement of staggered magnetization around a Zn impurity, which is related directly to the real part of the spin susceptibility $\chi(q)$ at $q=Q_{AF}$.[10] The asymptotic part of $\chi'(Q_{AF})$, which is responsible for the Cu, O, and Y NMR broadening, has always been estimated with the value of $\chi(q)$ *in the host*.[8–10] This same, unchanged value also determines T_{2G}.

V. COMPATIBILITY BETWEEN ^{89}Y, ^{63}Cu, AND ^{17}O NMR DATA

The last argument against an enhanced staggered magnetization, invoked in Ref. 1 but previously developed in Ref. 2, is that ^{89}Y NMR spectra show two Zn-induced lines, both at a frequency lower than that of the main line, while Williams and co-workers expect additional lines on both sides of the main line or a symmetric broadening of this main line. Williams and Krämer conclude that "It is not possible to account for the ^{89}Y NMR data within the enhanced antiferromagnetic correlations model."

In this paragraph, we show, only from a qualitative inspection of NMR data, that this statement is not correct. The location of ^{89}Y satellite lines indicates that the magnetic moment on $\mathrm{Cu_{NN}}$ and on $\mathrm{Cu_{NNN}}$ (the next nearest neighbors) is much larger than that on sites located farther from the impurity. However, the main ^{89}Y NMR line (sites which are neither $\mathrm{Cu_{NN}}$ nor $\mathrm{Cu_{NNN}}$) definitely broadens with Zn doping.[6] This demonstrates immediately that the perturbation is not limited to $\mathrm{Cu_{NN}}$ and $\mathrm{Cu_{NNN}}$, but affects the "bulk" as well, albeit with a lower magnitude. In the example of ^{63}Cu NMR [this nucleus has a much larger hyperfine coupling and a smaller averaging effect than ^{89}Y (Ref. 23)], in underdoped $\mathrm{YBa_2Cu_3O_{6+x}}$, the width of the ^{63}Cu NMR central line increases by a factor of 5 between room temperature (RT) and 80 K, and by a factor of 10 between RT and 24 K.[10] It is impossible to explain such a strong effect with a perturbation which does not extend further than the first and second neighbors to Zn [these represent less than 15% of the total number of sites in Ref. 10 with 1.5% Zn/Cu(2)]. One may wonder why the $\mathrm{Cu_{NN}}$ and $\mathrm{Cu_{NNN}}$ sites, which cause isolated ^{89}Y NMR lines, have never been identified in ^{63}Cu and ^{17}O NMR spectra. In fact, because of the large moment on $\mathrm{Cu_{NN}}$, such lines must be severely shifted in the tails of broad and complex (quadrupolar split) spectra, making them difficult to identify. Furthermore, $\mathrm{Cu_{NN}}$ and $\mathrm{O_{NN}}$ sites may experience wipeout and changes in both the quadrupole and hyperfine coupling tensors. Because the magnitude of these changes remains unknown, it is difficult to predict accurately where these weak resonances should be located. Recently, Ouazi *et al.* also noted that different nuclei probe the polarization at different length scales.[11]

Next we show briefly that calculations provide quantitative confirmation of the staggered magnetization model. Figure 1 shows ^{63}Cu, ^{17}O, and ^{89}Y NMR data taken in the same $\mathrm{YBa_2Cu_4O_8}$ sample, at the same temperature ($T=50$ K), and in the same magnetic field ($\mathrm{H_0}=14.0$ T). The magnetization

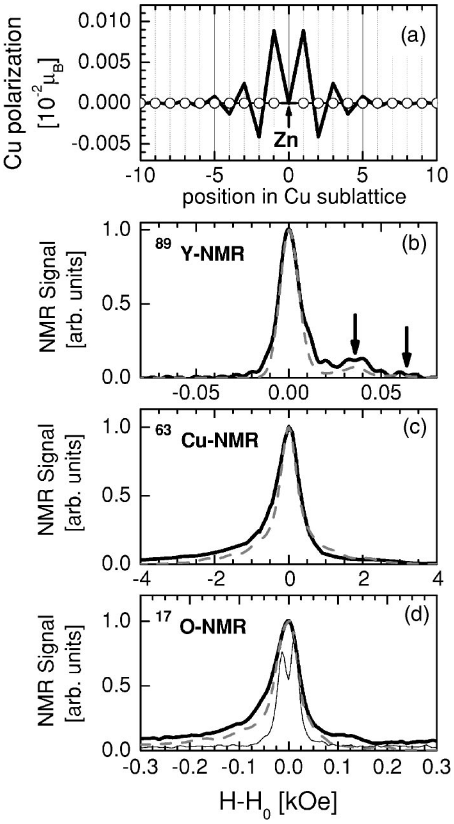

FIG. 1. (a) Quantitative model of staggered magnetization around a Zn impurity (1D cut for clarity; details in Ref. 12). (b), (c), and (d) ^{89}Y, ^{63}Cu, and ^{17}O NMR lines in YBa$_2$Cu$_4$O$_8$, doped with 1% of Zn per planar Cu, at T=50 K and with $H_0(\|c)$=14.0 T (continuous lines, from Ref. 12), together with the hyperfine field distribution (dashed lines) computed from the model in (a) using hyperfine coupling constants taken from the literature.

profile of a model of staggered polarization is shown in the upper panel. It is clear that the distribution of hyperfine fields computed from this model explains quantitatively the ^{63}Cu, ^{17}O, and ^{89}Y data (see Ref. 12; details will be published elsewhere). Remarkably, a staggered magnetization including a large moment on Cu$_{\mathrm{NN}}$, combined with the hyperfine coupling of ^{89}Y, produces two satellite lines, both on the high-field (low-frequency) side of the main line (arrows in Fig. 1). These results, obtained in a stoichiometric compound, are in agreement with the interpretation of ^{89}Y NMR spectra accepted for years[6] and with the recent work of Ouazi *et al.* in YBa$_2$Cu$_3$O$_{6+x}$.[11]

VI. OTHER REMARKS

The enhancement of the staggered magnetization on many Cu sites around Zn impurities in YBCO is supported by ^{63}Cu, ^{89}Y NMR, and ^{17}O NMR measurements.[6,8,9] We are not aware of any experimental report conflicting with these data. A proof of the staggered character of the spin polarization (already suggested in Refs. 8 and 9) was proposed in Ref. 10. To our knowledge, no counterargument has yet been put forward.

Williams and Krämer suggest that the results of Ref. 10 might be questionable because the contribution to the signal from the Cu chains was subtracted. However, both the raw data [Fig. 1(c) in Ref. 10] and the discussion of Ref. 10 demonstrate that the Cu(2) line broadening is undoubtedly *not* related to the Cu(1) chain signal. Furthermore, Fig. 1 shows results for Zn-doped YBa$_2$Cu$_4$O$_8$, in which there is no overlap between Cu(2) and Cu(1) signals.[12]

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