

Spin dynamics in the $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ system: Estimation of the rate of spin fluctuations

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We estimate the rate of fluctuations as 10^{11} sec^{-1} in the normal state of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ assuming that the spin fluctuations are the primary source of relaxation phenomena affecting the shape of the Mössbauer peaks. In the oxygenated and nonsuperconducting compound, the magnetic order is quasistatic rather than static as is generally believed. The spin clusters fluctuate at an approximate rate of 10^9 sec^{-1} below the Néel temperature. These findings may bear on the possible correlation between antiferromagnetic spin fluctuations and superconductivity. [S0163-1829(96)05946-2]

INTRODUCTION

Doping of the parent compounds, La_2CuO_4 , Nd_2CuO_4 , and $\text{YBa}_2\text{Cu}_3\text{O}_6$, destroys long range magnetic order and induces superconductivity. However, dynamical spin correlations survive in the superconducting materials as shown by neutron scattering experiments,¹⁻³ by NQR, NMR,⁴ and Raman scattering.⁵ The relationship between these antiferromagnetic spin fluctuations and the superconductivity is not clear. More specifically, Matsuda *et al.*⁶ reported measurements of the static, instantaneous, and dynamic spin correlations in their neutron scattering studies of as-grown (i.e., oxygenated) and the deoxygenated single crystals of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4+\delta}$. This electron-doped system has the distinctive feature that the oxygenated material is nonsuperconducting; however, it exhibits superconductivity after a deoxygenation treatment in an inert ambient above 800 °C which results in removal of a minuscule amount of extraneous oxygen (about 0.02 per formula unit).⁷ Matsuda *et al.* observed in the oxygenated crystals a prominent Bragg peak characteristic of static magnetic ordering which diminished considerably on deoxygenation. Dynamic spin correlations were also observed in the as-grown crystals, but not in the superconducting material.

We have shown⁸ that the presence of a minuscule amount of oxygen results in the localization of the electrons donated by Ce^{3+} ions and produces spin clusters of about 100 Å size. We report here that the magnetic ordering in the oxygenated $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ is really of a quasistatic nature in contrast to the static magnetic order of the parent Nd_2CuO_4 compound. We also estimate the rate of magnetic fluctuations in the oxygenated material, and more importantly, in the normal state of the superconducting material.

EXPERIMENT

Pellets of Nd_2CuO_4 and $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ were doped with ^{57}Co by allowing the carrier-free ^{57}Co activity to diffuse

into the material at about 900 °C in an oxygen atmosphere.¹⁰ Deoxygenation of samples was accomplished by the conventional thermal treatment at 850–875 °C for 20–30 h in argon flow. The cycle of oxygenation and deoxygenation both at 850–875 °C was repeated to check the reproducibility of experimental observations, and to ensure that ^{57}Co is sitting at the appropriate site(s). Mössbauer spectra were collected in a continuous flow cryostat tip below room temperature, and in a furnace above room temperature. A potassium ferrocyanide absorber with 0.25 mg/cm² of ^{57}Fe was used.

Several trial end error computer fits of the Mössbauer spectra at different temperatures using different models were attempted till a self-consistent picture emerged.¹⁰

RESULTS AND DISCUSSION

Oxygenated $\text{Nd}_2\text{Cu}(^{57}\text{Co})\text{O}_4$ and $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}(^{57}\text{Co})\text{O}_4$ below Néel temperature (T_N)

It was shown earlier⁸⁻¹⁰ that in the Nd-Cu(^{57}Co)-O system with or without Ce, a six-coordinate species, which we designate as *C*, is present only in oxygen rich antiferromagnetically ordered impurity regions. It cannot be eliminated by the conventional deoxygenation procedure and its abundance remains practically unchanged. This complicates the analysis of the Mössbauer spectra and makes it difficult to get reliable information about the normal state of the superconducting phase as depicted by the five-coordinate species *B*.⁹

By a special sequence of thermal treatments of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}(^{57}\text{Co})\text{O}_4$ (which consists of heating at 1050 °C in oxygen for several hours, then lowering the temperature to 900 °C and switching to nitrogen flow for 20 h followed by a conventional oxygenation-deoxygenation cycle), we have succeeded in eliminating the impurity phase in which species *C* resides. The spectra consist predominantly of species *B* which resides in the potentially superconducting phase with only 8% of a doublet in an uncharacterized phase (designated as *E*). In the oxygenated material,

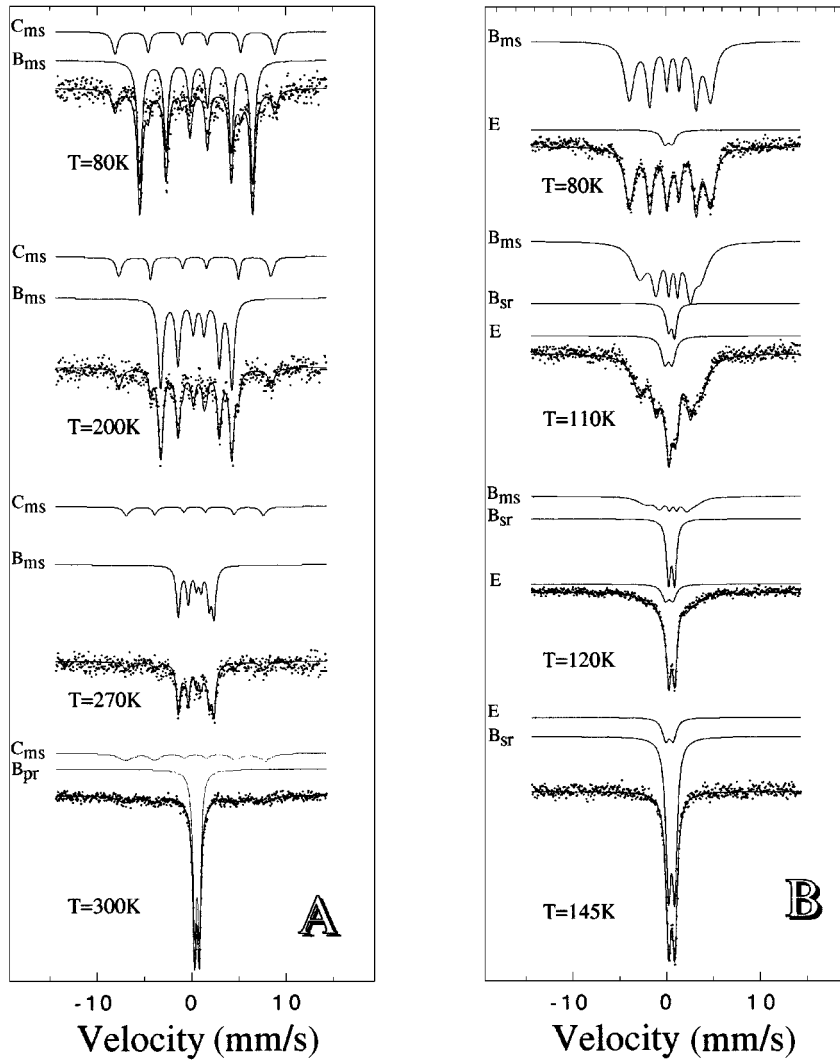


FIG. 1. Emission Mössbauer spectra at different temperatures of oxygenated (a) $\text{Nd}_2\text{Cu}^{(57)\text{Co}}\text{O}_4$ and (b) $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}^{(57)\text{Co}}\text{O}_4$. For the sake of clarity C_{sr} and impurity species D have been subtracted after fitting, ms: magnetically split; pr: paramagnetically relaxed; sr: superparamagnetically relaxed. B : five-coordinated species present in potentially superconducting phase. C : six-coordinated species present in oxygen-rich impurity phase.

the electron donated by Ce^{3+} is localized by an extraneous oxygen situated at an apical site with respect to a Cu atom in the Cu-O plane⁸⁻¹¹ and consequently species B is magnetically split into a sextet at low temperatures [Fig. 1(b)]. On the other hand, in $\text{Nd}_2\text{Cu}^{(57)\text{Co}}\text{O}_4$, we could not eliminate C completely by the special sequence of thermal treatments, and about 20% of C persists mainly as a supermagnetically relaxed species C_{sr} (Fig. 2).⁸ For the sake of clarity and ease of comparison of the behavior of Ce-free and Ce-containing materials as a function of temperature, especially in the close proximity to T_N , C_{sr} and an impurity species D (seen in Fig. 2) were subtracted after fitting, from all the spectra presented in Fig. 1(a).

Comparison of Figs. 1(a) and 1(b) shows that both oxygenated samples exhibit magnetic order at low temperatures and undergo a transition into the paramagnetic state at Néel temperatures which are about 275 and 125 K for Ce-free and Ce-doped samples, respectively, in good agreement with published results.^{6,12} This confirms that the Mössbauer probe is situated at the appropriate lattice site and reflects faithfully the properties of the two different host materials. The difference is clearly brought out from the temperature evolution of the spectra in Figs. 1(a) and 1(b). $\text{Nd}_2\text{Cu}^{(57)\text{Co}}\text{O}_4$ shows a

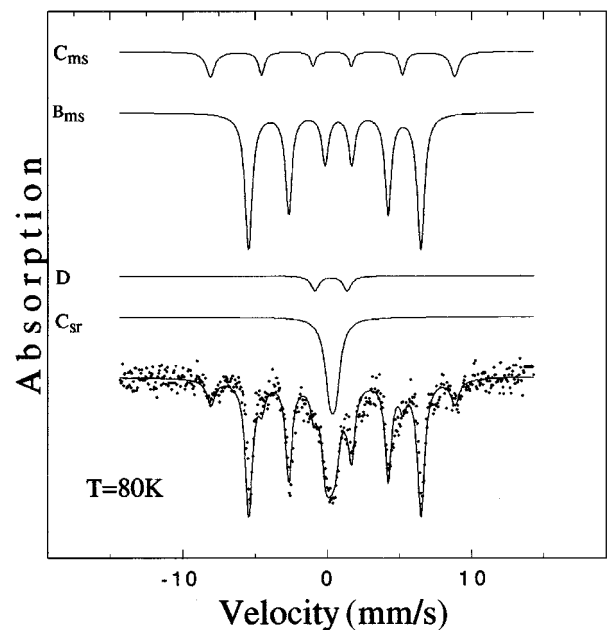


FIG. 2. Emission Mössbauer spectrum of $\text{Nd}_2\text{Cu}^{(57)\text{Co}}\text{O}_4$ at 80 K. C_{sr} and impurity species D are shown. ms: magnetically split; sr: superparamagnetically relaxed.

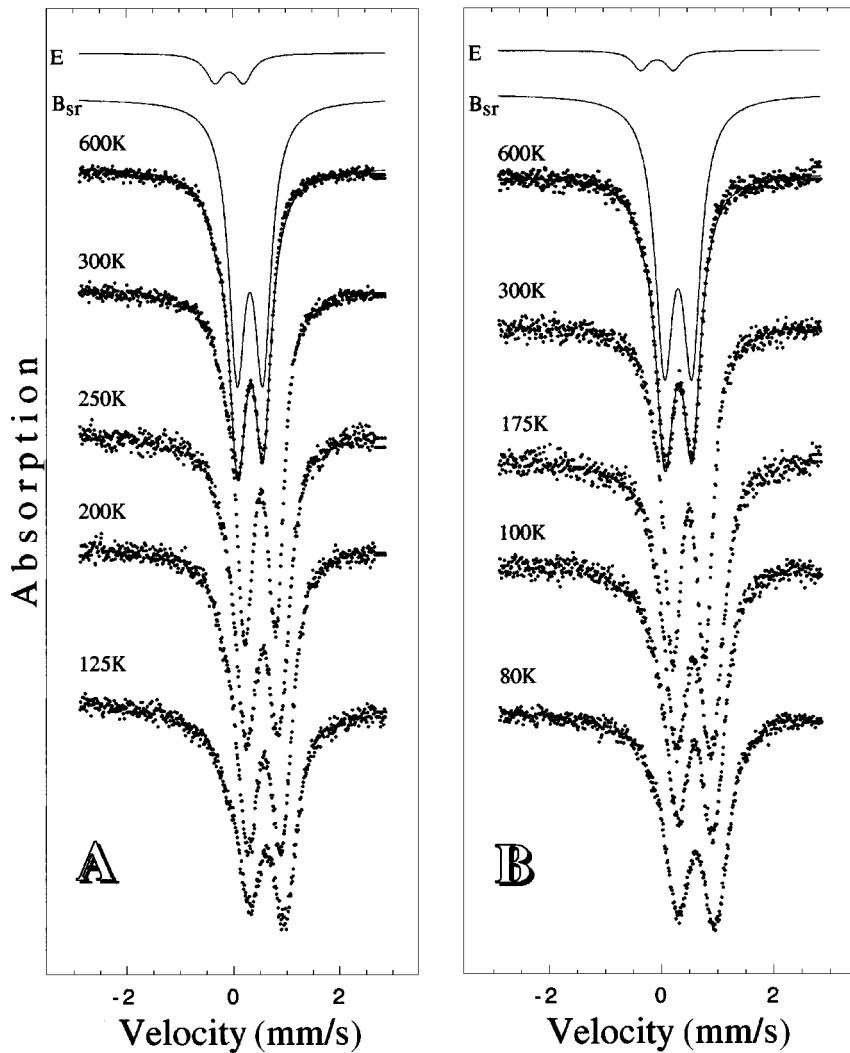


FIG. 3. Emission Mössbauer spectra of oxygenated (a) and deoxygenated (b) $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}^{(57}\text{Co})\text{O}_4$ at different temperatures. Decomposition of spectrum is shown only for 600 K. *B*: five-coordinated species present in potentially superconducting phase; *E*: impurity species.

regular temperature dependence of hyperfine magnetic field, with shapes and widths of peaks independent of temperature up to the complete paramagnetic collapse at T_N , as expected for compounds with static magnetic order [Fig. 1(a)]. Deoxygenation does not bring any significant change other than the Néel temperature.¹² Mössbauer spectra in Fig. 1(a) were fitted with the help of a computer program for the general case of combined hyperfine interaction with both magnetic and quadrupole terms being of comparable magnitude.¹³ We found that between 80 K and T_N , the electric field gradient (EFG) at the five-coordinate *B* site is positive and the angle between the main axis of EFG (V_{zz}) and internal magnetic field is 90° . Since the axes of the ordered magnetic moments are known from neutron scattering studies to be in the *a-b* plane,¹⁴ V_{zz} should be parallel to *c* axis.

In sharp contrast, the lines of the magnetically split sextet of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}^{(57}\text{Co})\text{O}_4$ are inhomogeneously broadened even at 80 K, and at higher temperatures, the magnetically split component coexists with its collapsed component which grows at the expense of the sextet with increasing temperature [Fig. 1(b)]. Such a superparamagnetic behavior is characteristic of variable size spin clusters as discussed earlier.⁸⁻¹⁰ An accurate computer fit of such spectra could not be accomplished because some important parameters are

not known, e.g., range of relaxation time τ associated with the size distribution of spin clusters, and spread in hyperfine internal fields presumably arising from doping with Ce. However, the main features of the temperature-dependent evolution of the spectra can be described quantitatively fairly well by a simple relaxation model¹⁵ modified to take into account the effect of superparamagnetism.¹⁰ We have obtained a good fit of all the spectra between 80 K and T_N . The fit gives a magnitude of the relaxation time τ of about 3×10^{-9} sec. One can assume that τ is not sensitively dependent on temperature below the Néel temperature. To put it in perspective, the fluctuation rates of the $\text{Cu}(2)$ derived molecular fields acting on the $^{170}\text{Yb}^{3+}$ probes in the nonsuperconducting oxygen deficient regions of $\text{Y}^{(170}\text{Yb})\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ at 1.4 K are a couple of orders of magnitude faster.¹⁶ In short, for the oxygenated (nonsuperconducting) $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}^{(57}\text{Co})\text{O}_4$, the magnetic ordering is not static. It behaves intrinsically as if it consists of a vast array of mesoscopic single domain spin clusters which are free to fluctuate at an approximate rate of 10^9 sec^{-1} below the Néel temperature.

The static magnetic correlations observed by Matsuda *et al.*⁶ presumably arose from oxygen rich impurity regions where species *C* resides.

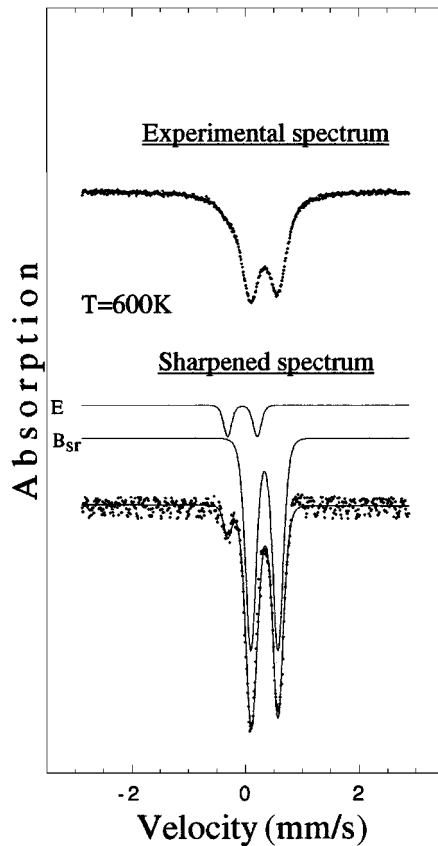


FIG. 4. Emission Mössbauer spectrum of deoxygenated $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}^{(57}\text{Co})\text{O}_4$ after fourth degree of sharpening (Ref. 17).

**Deoxygenated and oxygenated $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}^{(57}\text{Co})\text{O}_4$
above T_N**

A few representative Mössbauer spectra of an oxygenated and deoxygenated sample of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}^{(57}\text{Co})\text{O}_4$ recorded in a narrow velocity range at different temperatures are shown in Figs. 3(a) and 3(b). Decomposition of spectra taken at 600 K only is shown, as the spectra at other temperatures are similar. The decomposition is quite straightforward; all spectra consist of about 8% of species *E* and the remaining 92% of *B*.

The main feature of these spectra is the variation of the doublet asymmetry and linewidth with temperature [Figs. 3(a) and 3(b)]. One can see that at lower temperatures, the right component is more prominent than the left component and the peaks are broadened. At higher temperatures, the lines become narrower and the sign of asymmetry reverses (i.e., the left peak becomes more intense). The apparently asymmetric spectra at higher temperatures (above about 200 K for the deoxygenated sample and about 400 K for the oxygenated one) can be decomposed into two symmetrical doublets, impurity species *E* and the main doublet *B* [Figs. 3(a) and 3(b)]. The abundance and parameters of species *E* were reliably estimated by careful analyses of the spectra of the oxygenated material at 80 K, recorded both in wide [Fig. 1(b)] and narrow velocity scale [Fig. 3(a)] and in conjunction with the 600 K spectra of both samples where the *B* doublet is completely relaxed and therefore symmetrical (Fig. 3). These parameters were further confirmed by sharpening¹⁷ of the 600 K spectra using a fourth degree of sharpening and

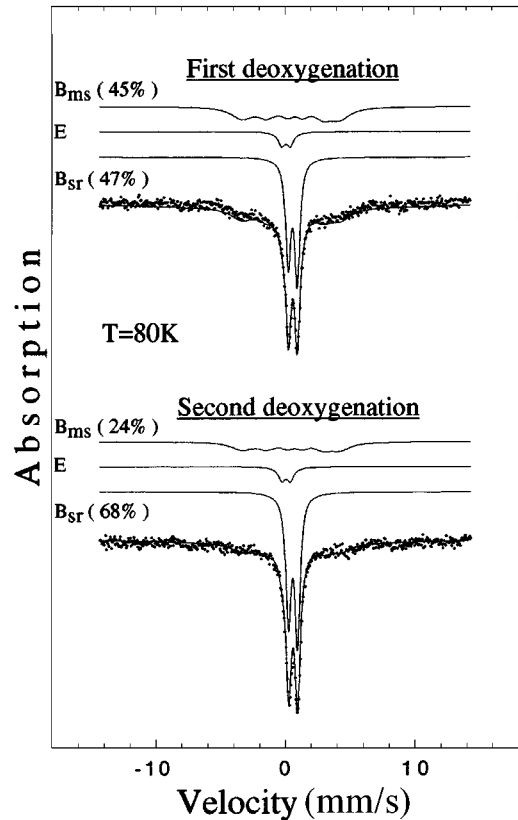


FIG. 5. Emission Mössbauer spectra of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}^{(57}\text{Co})\text{O}_4$ after one and two stage deoxygenation. B_{ms} and B_{sr} are five-coordinated species residing in nonsuperconducting and superconducting regions, respectively. ms: magnetically split; sr: superparamagnetically relaxed.

then fitting of sharpened spectra with two doublets of a fourth degree Lorentzian line shape (Fig. 4). Computer analysis showed that abundance and line shape of species *E* are not affected by temperature and oxygen content. Therefore, the change of the sign of asymmetry with temperature must be attributed exclusively to the temperature dependence of the asymmetry of species *B* which correlates with linewidth behavior; i.e., the increase in asymmetry is accompanied by line broadening. While considering the peak asymmetry of the relaxed doublet *B* at low temperatures, the contribution of the magnetically split B_{ms} (Fig. 5) was taken into consideration during the computer analysis.

The asymmetry of the doublet peaks can arise from the presence of an axial texture in the pellet, anisotropy of the recoil-free fraction (Goldansky-Karyagin effect), and from a relatively slow spin relaxation process. The axial texture was ruled out by measurements at the ‘magic angle’ ($\sim 55^\circ$) geometry at 600 K). Moreover, texture cannot account for the temperature dependence of the asymmetry. The Goldansky-Karyagin effect predicts an asymmetry increase with temperature, which would be the reverse of what we observe. Consequently, we are left with only one plausible explanation, namely a relatively slow spin relaxation process which accounts for both the line shape and linewidth behavior observed here. The same fitting procedure which was used for fitting of spectra of the oxygenated Ce-doped material below T_N (discussed earlier) gives a correct sign of the

asymmetry of the peaks for species B with a positive V_{zz} , which is in harmony with the Ce-free sample fit. Also, the relaxation time for both materials was found to be temperature dependent, and its approximate value for superconducting sample at $T=100$ K is estimated to be $\tau=5\times 10^{-11}$ sec. Assuming magnetic fluctuations as the major source of relaxation, one can say that the rate of magnetic fluctuations are of the order of 10^{11} sec $^{-1}$. We also find that the fluctuation rate in the potentially superconducting regions is not dependent on the density of the nonsuperconducting spin clusters as estimated by the amount of B_{ms} in Fig. 5. The rate was not affected when the proportion of spin clusters decreased from 45 to 24%.

In summary, the rate of spin fluctuations in the normal state of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}^{(57}\text{Co})\text{O}_4$ was estimated from the tem-

perature dependence of the linewidth and asymmetry of the Mössbauer quadrupole doublet. This is a report of an estimate of the rate of magnetic fluctuations in the normal state, and is likely to have theoretical ramifications. Also, the magnetic ordering in the oxygenated and nonsuperconducting $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ (free from magnetic impurities) is found to be quasistatic rather than static as reported earlier.

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