Double-resonance NMR probes of structural distortions in alkali-metal−fulleride superconductors

C. H. Pennington, C. Hahm, V. A. Stenger, K. Gorny, C. H. Recchia, and J. A. Martindale
Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio 43210

D. R. Buffinger and R. P. Ziebarth
Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210
(Received 7 May 1996; revised manuscript received 18 June 1996)

The ^{87}Rb NMR line shape of the Rb_3C_{60} superconductor contains three distinct peaks: one associated with octahedrally coordinated Rb in the fcc lattice of C_{60} molecules and two others, labeled T and T', both associated with tetrahedrally coordinated Rb. This contrasts with the accepted crystal structure, in which all tetrahedral Rb sites are equivalent. We report multinuclear single and double resonance NMR experiments which probe for effects which could lead to the unexpected splitting, and discuss implications for electronic structure. [S0163-1829(96)51334-2]

In the widely accepted fcc crystal structure[1] of the Rb_3C_{60} superconductor[2] two Rb^+ ions per C_{60} molecule occupy interstitial sites of tetrahedral (T) coordination, and one occupies a site of octahedral (O) coordination, leading one to expect two ^{87}Rb line shape features with an intensity ratio 2:1. Walstedt *et al.*[3] confirmed this expectation for high temperature (>300 K) NMR but found that at lower temperatures the peak associated with the tetrahedrally (T) coordinated Rb ions split into two peaks, T and T', with intensity ratio 11:2. This robust splitting necessarily implies a structural distortion or defect in these materials which is not detected by other probes. Walstedt *et al.* described several possibilities, including C_{60} molecular misorientations near the T' sites, displacements of the octahedral alkali ions away from the center of the octahedral cage toward the T' sites, C_{60}^{3-} molecular Jahn-Teller distortions, and charge density waves or distortions associated with the above. Alternatively, Fischer *et al.*[4] present x-ray-diffraction evidence that the alkali fullerides are off stoichiometric ($Rb_{3-x}C_{60}$, with $x\sim 0.03$) and suggest that T' sites may be nearest neighbors of tetrahedral vacancies. This agrees with the hypothesis of Lof *et al.*[5] that stoichiometric Rb_3C_{60} is a Mott insulator and that metallic behavior arises only from off-stoichiometry. Any of these possibilities would have major behavior implications for electronic structure and superconductivity; thus, it is crucial to probe directly for their existence. In this paper we report multinuclear double resonance NMR experiments which demonstrate that the magnitude of each of these effects is either vanishing or below very strict upper bounds.

Figure 1 shows alkali-metal-atom NMR line shapes for K_3C_{60} (^{39}K, $T_c=18$ K), Rb_3C_{60} (^{87}Rb, $T_c=29$ K), and Cs_2RbC_{60} (^{133}Cs, $T_c=33$ K), obtained by Fourier transform of the spin-echo signal. ^{87}Rb line shapes (for Rb_3C_{60}) contain the features identified previously[3] and labeled O, T, and T'. The same features, O, T, and T' are also observed in the ^{39}K and ^{133}Cs line shapes for K_3C_{60} and Cs_2RbC_{60}; thus, the T,T' splitting is a universal feature of the A_3C_{60} superconductors (with $A=$ K, Rb, or Cs). It should be noted further, finer resolution splittings of both the O and T peaks have recently been observed in ^{87}Rb spectra obtained using

magic angle spinning; here we address only the three peaks which are resolved in the static spectra.

In order to characterize possible differences in the local environments of the T and T' sites we have performed spin-echo double resonance (SEDOR)[7,8] experiments, at $T=80$ K and at magnetic field 8.8 T, on a sample of Rb_2CsC_{60} used in previous experiments.[9–11] In Rb_2CsC_{60} the Rb atoms occupy only the tetrahedrally coordinated interstitial sites, while the larger Cs ion occupies the more spacious octahedral site.[10,12] In the SEDOR experiment we first apply the usual spin-echo sequence—a $\pi/2$ pulse covering both the T and T' ^{87}Rb (the "α" species), followed after a time τ by a π pulse. The echo occurs at time 2τ following the initial $\pi/2$ pulse, and has an amplitude E. Individual contributions to E from both the T and T' sites (denoted E_T and $E_{T'}$) are resolved by Fourier transform. We follow the initial echo with a Carr-Purcell-Meiboom-Gill[13] train of 128 echoes in order to enhance signal to noise. Next, the spin-echo experiment is repeated; however, coincident with the π pulse on the α species (^{87}Rb T and T') we also apply a π pulse to a different nuclear species labeled "β." In this second spin-
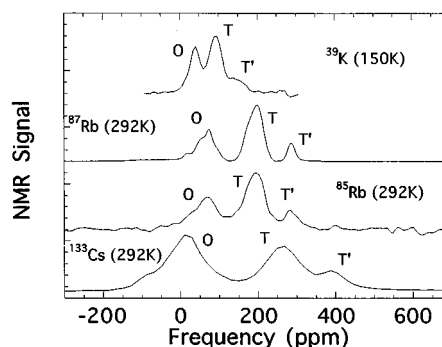

FIG. 1. ^{39}K, ^{85,87}Rb, and ^{133}Cs NMR line shapes of K_3C_{60}, Rb_3C_{60}, and $RbCs_2C_{60}$, respectively, at the temperatures indicated. Line shapes contain the features labeled O, T, and T' associated with octahedrally (O) and tetrahedrally (T,T') coordinated alkali ions. The T, T' splitting first observed (Ref. 3) in Rb_3C_{60} is present for the K and Cs doped materials as well.
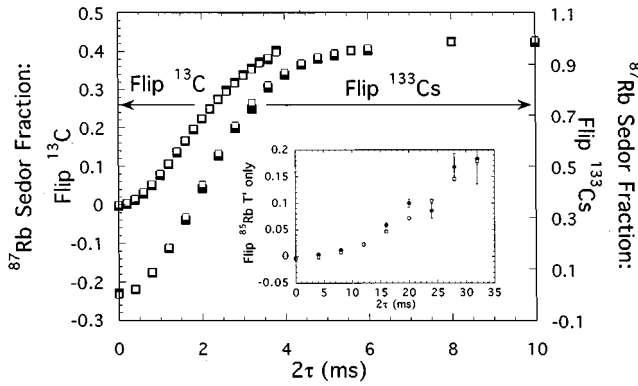
FIG. 2. Comparison of ^{87}Rb T (white squares) and T' (black squares) SEDOR fractions vs pulse spacing 2τ, at $T=80$ K and applied field $B=8.8$ T. Data sets are shown for $\beta = ^{13}$C, ^{133}Cs, and ^{85}Rb T' (inset), where β is the nuclear species which is flipped (see text).

echo sequence the echo amplitudes for species α is typically reduced, since the effect of α-β dipolar coupling is not refocused at the time of the echo. This reduction is characterized by the ''SEDOR fraction,'' defined as follows:

$$\text{SEDOR fraction } (T \text{ site}) = \frac{E_T(\text{no flip}) - E_T(\text{flip } \beta \text{ spin})}{E_T(\text{no flip})}. \quad (1)$$

The SEDOR fraction and its τ dependence are used to characterize the distances and the abundance of β atoms which are near neighbors of T (or T'). Walstedt *et al.*[3] used selective pulses to perform SEDOR on ^{87}Rb alone, with, for example, α being the ^{87}Rb T site and β the ^{87}Rb O site, and thereby ruled out the possibility of phase segregation of T and T'. Our results on multiple nuclear species enable us to extend their conclusions.

Figure 2 shows the SEDOR fraction vs 2τ for $\alpha = ^{87}$Rb T (open squares) and T' (blackened squares), and for $\beta = ^{13}$C, ^{133}Cs, and ^{85}Rb T' (inset). The striking feature for all three sets of data in Fig. 2 is that the SEDOR fractions for $\alpha = T$ and T' ^{87}Rb are remarkably similar, indicating that the T and T' environments, at least in terms of the configuration of nearby Cs, C, and T' Rb atoms, are also remarkably similar. For quantitative analysis we use the ''method of moments'' approach.[13] One can show that for early values of $t=2\tau$ the SEDOR fraction is given approximately by SF$=(1/2)\Delta^2 t^2 + O(\Delta^4 t^4)$. Here Δ^2 is given for a powder sample by:

$$\Delta^2 = (f)\text{NA}\frac{4}{5}\gamma_\alpha^2\gamma_\beta^2\hbar^2\left[\frac{1}{3}S_\beta(S_\beta-1)\right]\sum_i \frac{1}{r_i^6}, \quad (2)$$

where γ is the gyromagnetic ratio, S_β is the spin of the β species, the sum runs over all β sites, and NA is the natural abundance of the β isotope. The factor f is the effective flipping fraction for the β species, equal to one for a perfect π pulse. We find that while it is difficult to extract Δ^2 from experiment with high precision due to the importance of higher order contributions, we can obtain high precision comparisons of the very similar sets of T and T' data in Fig. 2 by scaling the time axis of one data set to best fit the other.

The SEDOR time development should scale approximately with $1/\sqrt{\Delta^2}$. We use this procedure to estimate the small percentage differences in Δ^2 for the T and T' curves.

First consider the case that ^{13}C is the β species (Fig. 2). Walstedt *et al.* suggested, as one of several possible T, T' splitting mechanisms, that the T' Rb could be facing a five membered C ring on each of the neighboring C$_{60}$'s, while in the accepted structure (which does include ''merohedral disorder,'' in which C$_{60}$ randomly assumes one of two possible orientations) all T sites would face 4 six membered rings. We calculate that Δ^2 (summing over the 240 carbons in the four near-neighboring C$_{60}$'s) is some 5.1% larger for the five membered configuration (1.68/ms^2) than for the six membered (1.60/ms^2). (Here we have used $f=0.8$, which we have calculated using the Bloch equations, the measured ^{13}C line shape, and the measured rf field strength.) The time scales of the T and T' experimental SEDOR curves, however, differ by only 0.3% $\pm$ 0.5%, indicating that Δ^2 for the two curves are equal to within 1%, much less than the difference between the five membered and six membered configurations. The carbon environments of the T and T' sites, then, are very nearly identical.

Walstedt *et al.* suggested another possible structural distortion leading to the T, T' splitting: that all four octahedral Rb (Cs, in our case) ions which are near neighbors of a Rb T' site are displaced from the center of their cages towards the T' sites; from this configuration one predicts an NMR intensity ratio for T to T' of 7:1, not far from experiment. The two remaining sets of SEDOR data in Fig. 2, however, rule out this splitting mechanism. The data sets shown use ^{87}Rb T and T' as the α nucleus, and ^{133}Cs and ^{85}Rb (T') (inset), respectively, as the β nucleus. The $\alpha = ^{87}$Rb T; $\beta = ^{133}$Cs SEDOR is quite similar to that of $\alpha = ^{87}$Rb T'; $\beta = ^{133}$Cs, but we find that its decay is some 3% $\pm$ 0.5% *faster* (indicating T-O distances *shorter* than those of T'-O). This small difference could suggest that octahedral Cs ions are displaced from the centers of their cages by a very small distance, approximately 1% of the expected T-O distance of 0.62 nm, but displaced *away* from, rather than toward, the T' Rb sites, a slight modification of the proposed structure of Walstedt *et al.* However, if this structure were correct, then tetrahedrally coordinated Rb which are nearest neighbors (i.e., displaced by a distance $a/2$) of the T' Rb would necessarily be T Rb, not T'. In that event one would expect that, for $\beta = ^{85}$Rb T', the $\alpha = ^{87}$Rb T' SEDOR fraction would develop substantially slower with 2τ than that of $\alpha = ^{87}$Rb T because a T' site could have no T' near neighbors. The data, however, confound this expectation; Fig. 2 (inset) shows that their SEDOR developments are the same, within experimental error of $\sim$5% (in time scale). Thus, a T' site has the same average number of T' neighbors (within $\sim$10%) as a T site. One must conclude that the T,T' splitting is not the result of displacement of the four T'-neighboring octahedral ions from the centers of their cages. Similar reasoning rules out the possibility suggested by x-ray-diffraction results of Fischer *et al.*[4] and NMR of Zimmer *et al.*[6] that T' sites are nearest neighbors (displaced by a distance $a/2$) to a tetrahedral site vacancy occuring off-stoichiometric Rb$_{3-x}$C$_{60}$. One can show that such a ''clustered'' arrangement of the T' sites around the vacancy

TABLE I. Experimentally and theoretically determined values of Δ^2, characterizing the dependence of the SEDOR fraction on the pulse spacing, as defined in the text [Eq. (2)]. The α nucleus (second column) is observed while the β nucleus (first column) is flipped. The parameter f, the flipping fraction, appearing in Eq. (2) is taken to be 0.80 for $\beta = {}^{13}\text{C}$, 1.0 for $\beta = {}^{133}\text{Cs}$, and measured directly as 0.130 for $\beta = {}^{85}\text{Rb} \; T'$ (here defined as a fraction of the total ${}^{85}\text{Rb}$ spectrum consisting of T and T'). In the fourth column (Theory) we have assumed that the pulse inverts populations for the full array of Zeeman levels, while in the fifth column we assume that only the central ($\frac{1}{2}, -\frac{1}{2}$) transition is flipped.

β Nucleus:	α Nucleus:	Δ^2 (ms^{-2}) (Exp.)	Δ^2 (ms^{-2}) (Theory)	Δ^2 (ms^{-2}) (Theory$'$)
${}^{13}\text{C}$	${}^{87}\text{Rb} \; T$	0.17 ± 0.02	0.160	0.160
	${}^{87}\text{Rb} \; T'$	0.17 ± 0.02		
${}^{133}\text{Cs}$	${}^{87}\text{Rb} \; T$	0.272 ± 0.01	2.74	3.27×10^{-2}
	${}^{87}\text{Rb} \; T'$	0.264 ± 0.01		
${}^{85}\text{Rb} \; T'$	${}^{87}\text{Rb} \; T$	$(3.6 \pm 0.2) \times 10^{-4}$	8.72×10^{-4}	2.12×10^{-4}
	${}^{87}\text{Rb} \; T'$	$(3.8 \pm 0.4) \times 10^{-4}$		

would result in quite different behaviors for the two data sets in Fig. 2 (inset); the time scale for the $\alpha = {}^{87}\text{Rb} \; T$ would be some 33% faster than that for $\alpha = {}^{87}\text{Rb} \; T'$, in sharp contrast with experiment. The only plausible conclusion is that the placement of T' sites must be thoroughly random, with neither a tendency for T' sites to cluster nor to repel. This conclusion is certainly inconsistent with ordering, even short range, of a charge density wave.

Why, then, the slight difference (which we believe to be greater than our experimental error) in the $\alpha = {}^{87}\text{Rb} \; T$ and $\alpha = {}^{87}\text{Rb} \; T'$ SEDOR curves for $\beta = {}^{133}\text{Cs}$? If β is a quadrupolar nucleus (as are ${}^{133}\text{Cs}$ and ${}^{85}\text{Rb}$), and if only the central transition is flipped, then the factor $S_\beta(S_\beta - 1)/3$ in Eq. (1) is replaced by $1/[2(2S_\beta + 1)]$. It is also possible to obtain a result intermediate between these two limits if the strength of the rf field is of the order of the electric-field gradient interaction. Our best fits for Δ^2 for the cases where $\beta = {}^{133}\text{Cs}$ and $\beta = {}^{85}\text{Rb}$ do lie in between these calculated limits. We suspect that the slight differences in the two $\beta = {}^{133}\text{Cs}$ SEDOR curves may result from a small difference in the electric-field gradient interactions for ${}^{133}\text{Cs}$ neighboring T and T'. The predicted and experimentally derived values of Δ^2 are summarized in Table I.

Walstedt *et al.* suggest a third possible mechanism which could result in the observed ${}^{87}\text{Rb} \; T, T'$ splitting: that upon doping the C_{60}^{3-} molecule undergoes a Jahn-Teller distortion. Undoped C_{60} has two types of C-C bonds: those bordering two hexagons ("6-6" bonds), with length ~ 0.140 nm, and those bordering a hexagon and pentagon ("6-5" bonds), 0.145 nm. Were C_{60}^{3-} to undergo a Jahn-Teller distortion one would expect a different distribution of bond lengths, depending on the magnitude and the nature of the distortion. To test this possibility we have performed a ${}^{13}\text{C}$ NMR Carr-Purcell sequence on a ${}^{13}\text{C}$ enriched (13%) sample of Rb_3C_{60} at 8.8 T and 80 K, following the procedure developed by Yannoni *et al.*[14] to measure the bond lengths in undoped C_{60}. The initial ${}^{13}\text{C}$ spin echo is successively refocused by π pulses spaced apart by a time 2τ. The amplitudes of the successive echoes form a transient signal with a time evolution determined by ${}^{13}\text{C}-{}^{13}\text{C}$ dipole-dipole coupling, with effects of chemical and Knight shift anisotropy removed. The signal is Fourier transformed to yield the characteristic Pake

pattern, shown in Fig. 3 (inset), from which one may infer ${}^{13}\text{C}-{}^{13}\text{C}$ bond lengths. The large feature at zero frequency results from ${}^{13}\text{C}$ nuclei having no ${}^{13}\text{C}$ near neighbors. The remaining intensity consists of two Pake doublet patterns, peaked at frequencies 1.48 ± 0.05 kHz and 1.62 ± 0.05 kHz (Fig. 3), which are related to the C-C bond distance $R_{\text{C-C}}$ according to[14]

$$\nu = \pm 3\gamma^2 \hbar (1 - D)/8\pi R_{\text{C-C}}^3, \qquad (3)$$

where D is the duty cycle of the rf power used in applying the successive π pulses. For the pulse spacing used, 57.4 μs, and the pulse duration, 10.4 μs, we have $D = 0.181$. The inferred bond lengths are 142 ± 1.5 and 146 ± 1.5 pm—equal to the values in undoped C_{60}. Based on the rather clear resolution of these two distances from the data, we estimate
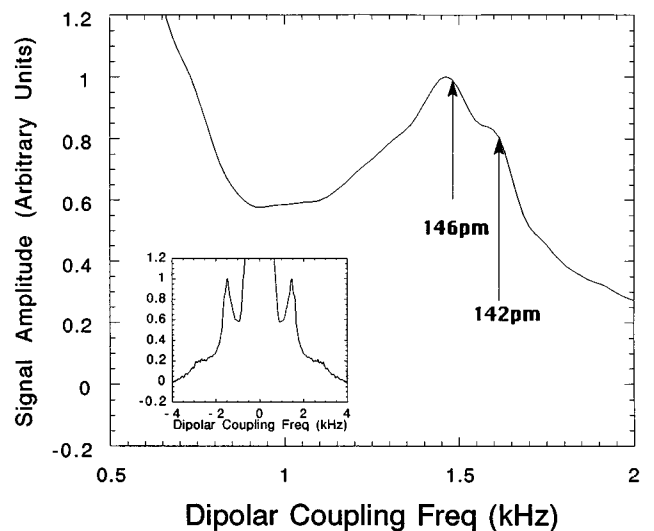

FIG. 3. Inset: Pake doublet pattern obtained by Fourier transform of the transient train of Carr-Purcell-Meiboom-Gill echoes for ${}^{13}\text{C}$ in 13% ${}^{13}\text{C}$ enriched Rb_3C_{60}, $T = 80$ K, $B = 8.8\text{T}$. Main figure: Detail of the inset, with arrows indicating the expected edges appearing in the Pake pattern for C-C bond lengths of 146 and 142 pm.
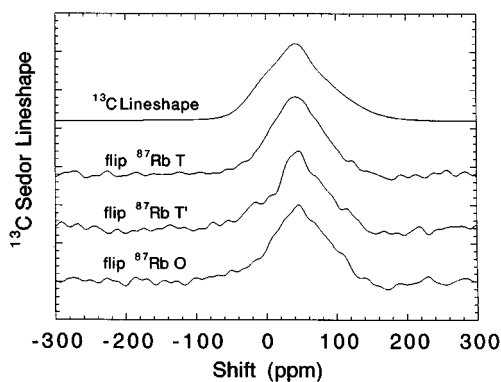
FIG. 4. ^{13}C line shapes of 13% ^{13}C enriched Rb_3C_{60}, $T = 80$ K and $B = 8.8$ T: Uppermost line shape is a conventional line shape from all ^{13}C spins. The lower three line shapes were obtained by SEDOR (see text) and result mostly from ^{13}C's which are nearest C neighbors of, respectively, the ^{87}Rb T, ^{87}Rb T', and ^{87}Rb O sites.

that any distortion of the C_{60}^{3-} ion must involve changes in the bond lengths which are smaller than ~ 0.002 nm.

Finally, if the ^{87}Rb T, T' splitting results from a difference in local spin density at the T and T' sites, one expects that ^{13}C which are near neighbors of T and T', respectively, would also experience different shifts. To test this proposition we perform $\alpha = {}^{13}$C and $\beta = {}^{87}$Rb T, T' and O SEDOR. We choose a time $\tau = 338$ μs, short enough such that the effects of ^{87}Rb-^{13}C dipolar coupling are small except for Rb-C pairs which are nearest neighbors. We take the ^{13}C spin echo with pulse spacing τ, then repeat the experiment, but flip selectively the T, T' or O peaks in the ^{87}Rb line shape. Subtracting the ^{13}C echo where the Rb T peak is flipped from the echo with no flip yields a ^{13}C signal derived primarily from ^{13}C's which are nearest neighbors of a Rb T site.[15,16] Results of this experiment, performed on a sample of Rb_3C_{60}, with 13% enrichment of ^{13}C, at a temperature of 80 K and a field of 8.8 T are shown in Fig. 4. The ^{13}C line shapes obtained for carbons near the Rb T, T' and O sites are

remarkably similar, with center of mass line positions at 39 ± 5, 42 ± 5, and 43 ± 5 ppm, respectively, relative to undoped C_{60}, and full widths at half maximum of 91 ± 5, 94 ± 5, and 97 ± 5 ppm. The conventional ^{13}C line shape without SEDOR has line position 38 ± 2 ppm and width 109 ± 2 ppm. (The slightly upward shifts and narrow linewidths for the SEDOR line shapes relative to the conventional may result from correlation between the ^{13}C-^{87}Rb dipolar coupling and ^{13}C shift anisotropies.) Although the ^{13}C shifts in thee materials are not completely understood,[10,17–24] it is surprising that there is no discernible difference in shifts between these structurally inequivalent ^{13}C sites.

Without information about the magnitudes of the structural distortions leading to the T, T' splitting in the alkali fullerides, theorists, in calculating electronic structures relevant for understanding superconductivity, have assumed the undistorted fcc lattice.[25] Our results would appear to validate that procedure. We show that T' sites are associated with neither misoriented C_{60} neighbors, displacements of the octahedral ions from the centers of their cages, nor hypothesized tetrahedral site vacancies. Any Jahn-Teller distortion of the C_{60}^{3-} ion involves C-C bond distance distortions of less than 1.5%. Clearly excess electron charge density is present at the T' sites, as that is the only plausible splitting mechanism, yet we demonstrate that the T' sites occupy the tetrahedral interstitial positions in a thoroughly random fashion, without site-to-site correlation. The effects of random T' placement on band structure should be much less pronounced than those resulting from the onset of an ordered charge density wave, where a gap in the density of states is formed. Despite these reassuring findings, the mechanism which results in the T, T' charge density distortion remains a mystery.

[1] P. W. Stephens *et al.*, Nature **351**, 632 (1991).

[2] See review, A. P. Ramirez, Supercond. Rev. **1**, 1 (1994).

[3] R. E. Walstedt *et al.*, Nature **362**, 611 (1993).

[4] J. E. Fisher *et al.*, J. Phys. Chem. Solids **56**, 1445 (1995).

[5] R. W. Lof *et al.*, Phys. Rev. Lett. **68**, 3924 (1992).

[6] G. Zimmer *et al.*, Phys. Rev. B **53**, 5620 (1996).

[7] D. Kaplan and E. L. Hahn, J. Phys. Radium **19**, 821 (1958).

[8] R. E. Walstedt and J. H. Wernick, Phys. Rev. Lett. **20**, 856 (1968).

[9] V. A. Stenger *et al.*, Phys. Rev. Lett. **74**, 1649 (1995).

[10] C. H. Pennington *et al.*, Phys. Rev. B **53**, R2967 (1996).

[11] D. R. Buffinger *et al.*, J. Am. Chem. Soc. **115**, 9267 (1993).

[12] V. A. Stenger *et al.*, Phys. Rev. B **48**, 9942 (1993).

[13] C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, New York, 1989).

[14] C. S. Yannoni *et al.*, J. Am. Chem. Soc. **113**, 3190 (1991).

[15] We thank Dr. R. E. Walstedt for suggesting this experiment.

[16] C. D. Makowka *et al.*, Phys. Rev. B **31**, 5663 (1985).

[17] R. Tycko *et al.*, Phys. Rev. Lett. **68**, 1912 (1992).

[18] R. Tycko *et al.*, Phys. Rev. B **48**, 9097 (1993).

[19] See review by, C. H. Pennington and V. A. Stenger, Rev. Mod. Phys. **68**, 855 (1996).

[20] H. Alloul *et al.*, Physica C **235-240**, 2509 (1994).

[21] G. Zimmer *et al.*, Europhys. Lett. **24**, 59 (1993).

[22] G. Zimmer *et al.*, Europhys. Lett. **27**, 543 (1994).

[23] M. Mehring *et al.*, Philos. Mag. B **70**, 787 (1994).

[24] R. Kerkoud *et al.*, Europhys. Lett. **25**, 379 (1994).

[25] See review, M. P. Gelfand, Supercond. Rev. **1**, 103 (1994).