

Role of Dynamic Jahn-Teller Distortions in Na_2C_{60} and $\text{Na}_2\text{CsC}_{60}$ Studied by NMR

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Through ^{13}C NMR spin lattice relaxation (T_1) measurements in cubic Na_2C_{60} , we detect a gap in its electronic excitations, similar to that observed in tetragonal A_4C_{60} . This establishes that Jahn-Teller distortions (JTD) and strong electronic correlations must be considered to understand the behavior of even electron systems, regardless of the structure. Furthermore, in metallic $\text{Na}_2\text{CsC}_{60}$, a similar contribution to T_1 is also detected for ^{13}C and ^{133}Cs NMR, implying the occurrence of excitations typical of JT distorted C_{60}^{2-} (or equivalently C_{60}^{4-}). This supports the idea that dynamic JTD can induce attractive electronic interactions in odd electron systems.

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It has been known, almost since the discovery of alkali doped fullerenes, that A_4C_{60} is insulating, while A_3C_{60} is metallic and superconducting [1]. This contrasts with expectations for a rigid band filling model, as the C_{60} lowest unoccupied molecular t_{1u} level should form a triply degenerate band. All A_nC_{60} with $n < 6$ should be either metals if the strength of the Coulomb repulsion U is small compared to the bandwidth W or Mott insulators if U is larger. In fullerides, U/W is close to the critical ratio where a metal-insulator transition is expected [2], but the observation of both metals and insulators within this family is puzzling.

An attractive explanation [3–5] is that the presence of Jahn-Teller distortions (JTD) of the C_{60} molecule could create *effective electronic interactions* which would modulate U , so that different compounds could be on different sides of the metal-insulator transition. More precisely, the computation of $U_{\text{eff}} = E(n+1) + E(n-1) - 2E(n)$, where n is the number of electrons per C_{60} , supports this idea, when the larger gain of electronic energy associated with the JTD of an evenly charged C_{60} ball is taken into account [3–5]. It follows that in even electron systems JT effects *add* to the Coulomb repulsion to localize electrons, whereas for odd electron systems they *oppose* the Coulomb repulsion and favor delocalization. To give some experimental support to this idea, a large amount of work has been devoted to the search of JTD in fullerides, but without success up to now. However, the distortion is expected to be very small and possibly dynamic, which makes it difficult to detect directly. Alternatively, recent models have suggested that the different properties between A_4C_{60} (body centered tetragonal) and A_3C_{60} (face cubic centered) are due to their different structures [6].

In order to sort out the relevant parameters for the physics of A_nC_{60} , we present here an NMR study of Na_2C_{60} and $\text{Na}_2\text{CsC}_{60}$, as they have the same *cubic* structure but *even* and *odd* stoichiometries. Na_2C_{60} is the only compound with $n = 2$ known so far, but experimental studies are still limited and controverted. The first ESR

studies [7] concluded that its electronic properties were identical to K_4C_{60} , but more recently another ESR investigation claimed that it was metallic with a metal-insulator transition at 50 K [8]. We present the first NMR study of Na_2C_{60} , which allows one to detect singlet-triplet excitations of JTD C_{60} balls, as found in A_4C_{60} [9–11]. This rules out a strong dependence of the electronic properties on the structure, as one expects similar properties for $n = 2$ and 4 due to electron-hole symmetry in the t_{1u} band. We then extend our investigation to $\text{Na}_2\text{CsC}_{60}$, which superconducts below $T_c = 12$ K [12]. In the metallic phase, we evidence an anomalous contribution to the ^{13}C and ^{133}Cs NMR spin-lattice relaxation rate $1/T_1$. As it is similar to that found in Na_2C_{60} , we assign it to the presence of Jahn-Teller distorted $\text{C}_{60}^{(2,4)-}$. This demonstrates the importance of dynamic JTD in metallic fullerides also and suggests that the metallic character of A_3C_{60} could be related to an enhanced stability of $\text{C}_{60}^{(2,4)-}$.

The Na_2C_{60} and $\text{Na}_2\text{CsC}_{60}$ samples were prepared by conventional solid-state reaction and checked by x ray. At high T , both compounds are isostructural to A_3C_{60} systems [face centered cubic structure (fcc) with space group $Fm\bar{3}m$], but they undergo below room T an orientational ordering transition like pure C_{60} [the symmetry is reduced to simple cubic (sc) with $Pa\bar{3}$ space group] [13,14]. NMR $1/T_1$ measurements were carried out in a 7 T field with usual saturation recovery sequences.

Figure 1 shows that $1/T_1$ for ^{13}C in Na_2C_{60} increases very steeply and can be fitted between 200 and 300 K by an activated law $1/T_1 \propto \exp(-E_a/k_B T)$ with $E_a = 140 \pm 20$ meV. This contrasts with the linear T dependence (the Korringa law) expected for simple metals [15] and indicates that a gap E_a separates the ground state from the excited states of the system. This is similar to the insulating A_4C_{60} systems, where an activated behavior dominates the relaxation with $E_a \approx 50$ –75 meV [9–11,16]. Besides this central fact, more features are evident as follows.

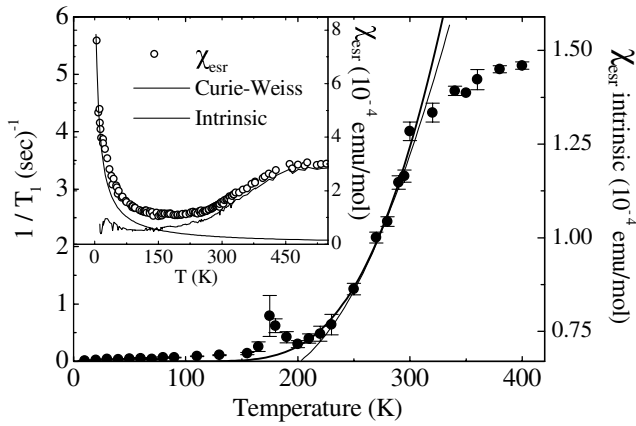


FIG. 1. ^{13}C NMR $1/T_1$ as a function of temperature in Na_2C_{60} . The thick line is a fit to an activated law with $E_a = 140$ meV. The thin line (right scale) is the intrinsic part of χ_{esr} . Inset: χ_{esr} in Na_2C_{60} decomposed into an intrinsic part and a Curie-Weiss contribution.

(i) There is a peak at 180 K which is typical of a contribution due to the slowing down of C_{60} molecular motions [17], as shown in more details elsewhere [18].

(ii) At low temperature, $1/T_1$ is enhanced with respect to the activated law. In Fig. 2, it can be more clearly seen that $(T_1 T)^{-1}$ tends to a constant value. If intrinsic, such a contribution could indicate a residual metallic character with a small density of states $n(E_f) \approx 1 \text{ eV}^{-1} \text{ spin}^{-1}$ [15]. A very similar behavior was in fact observed in Rb_4C_{60} , where an additional relaxation mechanism becomes efficient at low T , which was assigned to a small gap (≈ 20 meV) [10]. This gap is easily closed by applying pressure and a growing linear contribution to the relaxation is observed with increasing pressure *that coexists* with the activated contribution [10]. Within this frame, Na_2C_{60} would be equivalent to Rb_4C_{60} under an applied pressure of roughly 1 kbar.

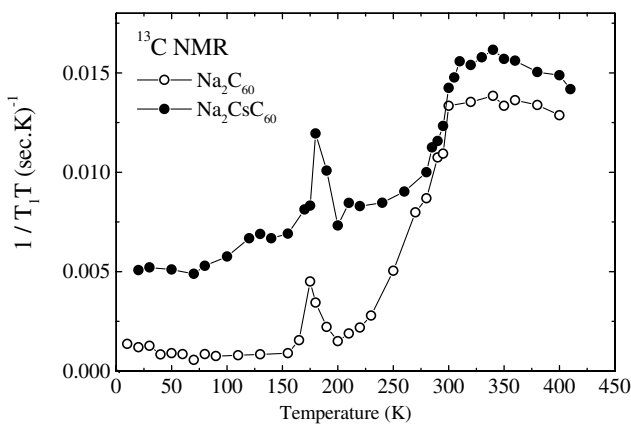


FIG. 2. $1/T_1 T$ for ^{13}C as a function of temperature in Na_2C_{60} and $\text{Na}_2\text{CsC}_{60}$. Below 200 K, the recovery curves for the NMR magnetization are not exponential and T_1 is defined as the mean value of a double exponential fit.

The relaxation behavior does not change down to 10 K, implying that there is no transition to an ordered ground state. In particular, we do not observe any anomaly at 50 K that might be assigned to a metal-insulator transition as claimed in Ref. [8]. Hence, the ground state is non-magnetic, which is further confirmed by the absence of magnetic broadening of the ^{13}C and ^{23}Na NMR spectra at low T [18]. This is again similar to A_4C_{60} .

(iii) Above 300 K, $1/T_1$ saturates, which would be expected only for $T \geq E_a/k_B \approx 1600$ K. As the structural transition from sc to fcc takes place at 310 K, one can wonder if there is, for example, a smaller gap in the fcc phase. Data at higher temperatures would be needed to conclude about this.

Like $1/T_1$, the ESR susceptibility χ_{esr} increases between 200 and 300 K [7]. As a quantitative comparison with NMR should give us further insight into the properties of the system, we have measured χ_{esr} in our sample (see the inset in Fig. 1), with results analogous to Ref. [7]. The intrinsic part χ_{int} of χ_{esr} is difficult to extract precisely below 250 K as a large Curie contribution is always observed in Na_2C_{60} . From a low T fit, we deduce a Curie-Weiss contribution $C/(T + T_n)$ with $T_n = 8$ K corresponding to 2.3% impurities per C_{60} . The remaining part χ_{int} tends to a constant value of $6 \cdot 10^{-5} \text{ emu/mol}$ at low T . If interpreted as a Pauli contribution in χ_{esr} , this term would be quantitatively consistent with the constant $(T_1 T)^{-1}$ found at low T . Conductivity data will, however, be needed to conclude about a possible weak metallicity of this compound. Figure 1 (right scale) evidences that the T dependent contribution χ to χ_{int} scales with $1/T_1$. The simplest way to relate $1/T_1$ and χ is to assume that both are associated with electronic excitations characterized by a spin correlation function with an exponential decay time τ . In the limit $\omega_e \tau \ll 1$, where ω_e is the electronic Larmor frequency, one expects [19]

$$\frac{1}{T_1} = \left(\frac{A}{\hbar}\right)^2 \frac{\chi}{N_A \mu_B^2} k_B T \tau, \quad (1)$$

where A is the hyperfine coupling and N_A is the Avogadro number. The limited T range of the experiment does not allow one to probe efficiently the T dependence of τ . Assuming that it is constant and using $A = 4 \times 10^{-20} \text{ erg}$ [15], we obtain $\tau \approx 8 \times 10^{-14} \text{ sec}$, which has the same order of magnitude as that found in Rb_4C_{60} and is consistent with $\omega_e \tau \ll 1$.

To summarize, we conclude that *there are strong similarities between Na_2C_{60} and A_4C_{60}* . To describe the weakness of the metallic character of these compounds, models involving a (dynamic) JTD of the C_{60} molecule are the most likely, as they naturally yield a non-magnetic ground state. Indeed, for $n = 1, 2, 4, \text{ or } 5$, a unimodal distortion of the C_{60} molecule lifts the degeneracy of the t_{1u} levels, leaving either a single nondegenerate ground state (this distortion “A” can be viewed as a disk flattening of the C_{60} along one axis) or two degenerate levels (case “B”, where

the molecule is instead elongated) [4]. For $n = 2$, A has the lowest energy, implying a singlet ground state, while B is a triplet because of Hund's rules and lies 130 meV higher in energy [4]. The value of this "spin gap" between A and B is very close to the 140 meV gap observed here in $1/T_1$, so that we can attribute the relaxation to singlet-triplet-like excitations that take place when one molecule goes from one distortion to the other. This means that in Eq. (1), τ corresponds to the spin lifetime of the thermally populated triplet state. While Ref. [4] predicts the same spin-gap for C_{60}^{2-} and C_{60}^{4-} , the experimental difference found in Na_2C_{60} and A_4C_{60} might result from excitations to higher electronic levels (t_{1g}), which breaks the electron-hole symmetry in t_{1u} [20]. Alternatively, it could be due to an influence of the local crystal symmetry, whose role is also suggested by the saturation in $1/T_1$ observed here at the structural transition.

The fact that molecular properties on an energy scale of 140 meV are not smeared out by the formation in the solid of bands of typically 500 meV width requires strong electronic correlations. This was recognized by Fabrizio *et al.* [21], who qualified these systems as "Mott Jahn-Teller insulators." They emphasized that the splitting between t_{1u} levels induced by the JT distortion, estimated to be 500 meV (and observed experimentally as an "optical gap" in A_4C_{60} [22,23]) is too small to form a band insulator. Electronic correlations increase the average time spent by one electron on a C_{60} ball, so that "molecular physics," such as the JT distortions, can take place even without complete localization. This model could then also explain the residual metallic character suggested by our low T data in Na_2C_{60} .

We now turn to the study of Na_2CsC_{60} , for which Fig. 2 shows $(T_1T)^{-1}$ compared with Na_2C_{60} . Below 150 K, $(T_1T)^{-1}$ in Na_2CsC_{60} is dominated by a T independent contribution, in agreement with its metallic character, which is nearly suppressed in Na_2C_{60} . But at higher T , $(T_1T)^{-1}$ departs from the metallic behavior and surprisingly, its overall behavior is very similar to that of Na_2C_{60} . We want to argue here that *this is not accidental* but reveals a similar relaxation mechanism in the two compounds. We restrict our discussion to the *sc* phase of Na_2CsC_{60} ($T < 300$ K), since it was recently suggested that the fcc phase might be insulating [24].

The strong deviation from the Korringa law in Na_2CsC_{60} had already been observed previously [25]. It was attributed to an increase of the density of states associated to the lattice expansion plus a peak due to molecular motions around 300 K. We present here new experimental data to refute this hypothesis. First, to avoid completely a contribution of the C_{60} molecular motions to the relaxation, we have performed measurements on ^{133}Cs which is not coupled to these motions. It can be checked in Figs. 2 and 3 that $(T_1T)^{-1}$ for ^{133}Cs does not exhibit any molecular motion peak around 180 K, contrary to ^{13}C . On the other hand, $(T_1T)^{-1}$ for ^{133}Cs does deviate

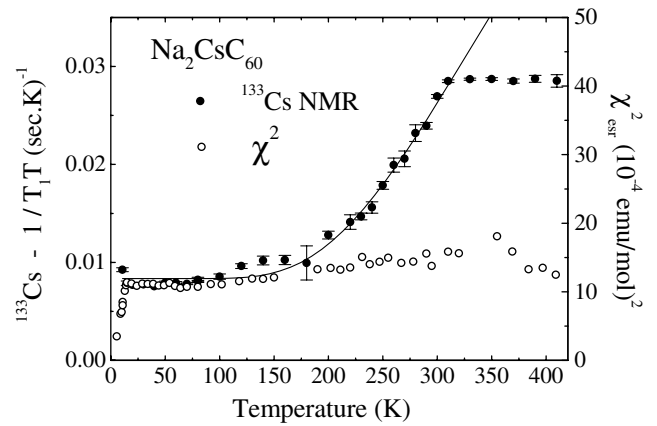


FIG. 3. Left scale: $1/T_1T$ for ^{133}Cs as a function of temperature in Na_2CsC_{60} . The recovery curves are exponential through the full T range. As shown by the line, the relaxation can be fitted by $1/T_1T = A + B/T^* \exp(-E_a/T)$ with $E_a = 110$ meV. Right scale: χ^2 as a function of T .

above 150 K from the Korringa law, as for ^{13}C , ensuring that this deviation is not due to molecular motions but to *electronic excitations*. Second, to determine an eventual $n(E_f)$ -related increase of $(T_1T)^{-1}$, we have measured χ_{esr} in our sample. It does not follow a simple Pauli law but increases slightly above 100 K. The increase of $(T_1T)^{-1}$ should scale with χ^2 , if both were related to a variation of $n(E_f)$ [15], but Fig. 3 shows that $(T_1T)^{-1}$ increases much more steeply, already at 200 K, well into the *sc* phase. Hence, *the increase of $(T_1T)^{-1}$ in Na_2CsC_{60} is related to an additional relaxation channel*. It can be fitted by an activated law with $E_a = 110 \pm 5$ meV, as sketched in Fig. 3.

It is then natural to propose that this additional relaxation mechanism is similar to that of Na_2C_{60} . For a JT distorted C_{60}^{3-} , there are no possibilities for singlet-triplet transitions directly similar to the ones of a C_{60}^{2-} . Therefore, we believe that the similarity between Na_2C_{60} and Na_2CsC_{60} comes directly from the presence of C_{60}^{2-} in Na_2CsC_{60} , or equivalently C_{60}^{4-} . This conclusion supports the idea that JTD enhance in odd electron systems the lifetime of C_{60}^{2n-} , formed when electrons jump randomly from ball to ball in the metal. As the gap observed by NMR in Na_2C_{60} is related to *individual* excitations of C_{60}^{2-} and not to a band gap, similar excitations might occur in Na_2CsC_{60} as well, if $C_{60}^{(2,4)-}$ exist within the metal for times τ_{pair} sufficiently long compared to the spin lifetime τ of an excited state. This does not imply a static charge separation, which can anyway be ruled out by ^{23}Na NMR spectra.

Using Eq. (1), τ can be extracted from $(T_1T)^{-1}$ if the singlet-triplet component in χ is known. We assume a similar T dependence as that found in Na_2C_{60} , which scales as $\chi = \alpha T^{-1} \exp(-E_a/T)$ in the experimental T range and the gap value $E_a = 110$ meV determined accurately from ^{133}Cs NMR. Such a contribution can only be smaller than the increase of χ_{esr} , which implies $\alpha \lesssim 2$

and yields $\tau \approx 10^{-14}$ sec. On the other hand, the time τ_{res} spent by one electron in the vicinity of one C_{60} , which is a lower limit for τ_{pair} , can be estimated by $\tau_{\text{res}} \approx \hbar n(E_f) \approx 6 \cdot 10^{-15}$ sec in $\text{Na}_2\text{CsC}_{60}$, which is only slightly shorter than τ . Electronic correlations, Jahn-Teller effects, as well as scattering on a C_{60} ball, would all increase τ_{res} compared to this simple estimate, so that we are likely in the limit $\tau_{\text{pair}} > \tau$ where the $\text{C}_{60}^{(2,4)-}$ can contribute to the NMR spin-lattice relaxation.

Both the gap value and τ are reduced compared with Na_2C_{60} . The same trend was observed in Rb_4C_{60} , where τ and the gap decrease with increasing pressure, i.e., increasing density of states [10]. This suggests a direct relation between τ and $n(E_f)$, which raises the question of the mechanism for the relaxation time τ of the triplet states. Such a trend would be expected if the triplet states are relaxed by conduction electrons, although the distinction is ambiguous since the triplet states are formed by “potential” conduction electrons. This would also predict that for higher density of states as in K_3C_{60} and Rb_3C_{60} , the contribution of triplet states to the relaxation almost disappear. We note that although a “better” Korringa law is observed in these compounds [26], a 20%–30% increase of $(T_1T)^{-1}$ was still noticed between 100 and 300 K. If it has a similar origin, the presence of $\text{C}_{60}^{(2,4)-}$ will be a common feature of metallic A_3C_{60} compounds.

In conclusion, we have shown that Na_2C_{60} has a non-magnetic ground state and that its low energy electronic excitations are characterized by a 140 meV spin gap. This is very similar to A_4C_{60} systems and supports the “Mott JT scenario” [21] to describe fullerides with two or four electrons per C_{60} . Furthermore, we evidence very similar electronic excitations in $\text{Na}_2\text{CsC}_{60}$, coexisting with typically metallic ones. In both cases, we assign the spin-gap to singlet-triplet excitations between two JT distortions of C_{60}^{2n-} balls ($n = 1$ or 2). Because the triplet state provides a very efficient relaxation mechanism for NMR, we could indirectly detect here for the first time the presence of dynamic JTD in a superconducting fulleride. Our study implies that $\text{Na}_2\text{CsC}_{60}$ undergoes charge fluctuations on a time scale of 10^{-14} sec, which create preferentially $\text{C}_{60}^{(2,4)-}$. We suggest that this can be rationalized as a consequence of the JTD which stabilizes evenly charged C_{60} .

A first indication of the role played by JTD in the electronic properties of fullerides was the observation in the metallic cubic quenched CsC_{60} of localized C_{60}^{2-} [27]. Although this difference in charge lifetime remains to be understood, these behaviors suggest that the key feature behind the physics of cubic fullerides is due to an interplay between strong electronic interaction and “JT mediated electronic interactions.” Electronic correlations are essential for molecular excitations, such as the JTD, to exist in the solid. JT mediated electronic interactions play in turn a crucial role in determining the insulating or metallic character of a given compound, by inducing repulsive

interactions in even electron systems and attractive interactions in odd electron systems, in order to promote the existence of C_{60}^{2n-} . The recent discovery of a way of doping continuously the $\text{C}_{60} t_{1u}$ level through a field-effect device might open a new path for checking this original behavior more systematically [28].

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- [1] R. C. Haddon *et al.*, *Nature (London)* **350**, 320 (1991).
 - [2] O. Gunnarsson, E. Koch, and R. M. Martin, *Phys. Rev. B* **54**, R11026 (1996).
 - [3] W. Victoroff and M. Héritier, *J. Phys. I (France)* **6**, 2175 (1996).
 - [4] N. Manini, E. Tosatti, and A. Auerbach, *Phys. Rev. B* **49**, 13008 (1994).
 - [5] O. Gunnarsson, *Phys. Rev. B* **51**, 3493 (1995).
 - [6] O. Gunnarsson, S. C. Erwin, E. Koch, and R. M. Martin, *Phys. Rev. B* **57**, 2159 (1998); J. E. Han, E. Koch, and O. Gunnarsson, *Phys. Rev. Lett.* **84**, 1276 (2000).
 - [7] P. Petit *et al.*, *Progress in Fullerene Research*, edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth (World Scientific, Singapore, 1994), p. 148.
 - [8] Y. Kubozono *et al.*, *Phys. Rev. B* **59**, 15062 (1999).
 - [9] G. Zimmer, M. Helme, M. Mehring, and F. Rachdi, *Europhys. Lett.* **27**, 543 (1994).
 - [10] R. Kerkoud *et al.*, *J. Phys. Chem. Solids* **57**, 143 (1996).
 - [11] G. Zimmer, M. Mehring, C. Goze, and F. Rachdi, *Phys. Rev. B* **52**, 13300 (1995).
 - [12] K. Tanigaki *et al.*, *Nature (London)* **356**, 419 (1992).
 - [13] T. Yildirim *et al.*, *Phys. Rev. Lett.* **71**, 1383 (1993).
 - [14] K. Prassides *et al.*, *Science* **263**, 950 (1994).
 - [15] In a metal, one expects $(T_1T)^{-1} = (\pi k_b/\hbar)A^2n(E_f)^2$. From the Korringa value at low T in $\text{Na}_2\text{CsC}_{60}$, we deduce a hyperfine coupling $A = 4 \times 10^{-20}$ erg, which lies with other estimates of A in fullerides within a factor of 4.
 - [16] We use here $E_a = E_g$ instead of $E_a = E_g/2$, as done in [9–11] by reference to a semiconducting model.
 - [17] Y. Yoshinari, H. Alloul, G. Kriza, and K. Holczer, *Phys. Rev. Lett.* **71**, 2413 (1993).
 - [18] V. Brouet *et al.*, in *Electronic Properties of Novel Materials—Molecular Nanostructures*, edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth, AIP Conf. Proc. No. 544 (AIP, New York, 2000), p. 24.
 - [19] R. M. White, *Quantum Theory of Magnetism* (Springer-Verlag, Heidelberg, New York, 1983).
 - [20] M. C. M. O’Brien, *Phys. Rev. B* **53**, 3775 (1996).
 - [21] M. Fabrizio and E. Tosatti, *Phys. Rev. B* **55**, 13465 (1997).
 - [22] M. Knupfer and J. Fink, *Phys. Rev. Lett.* **79**, 2714 (1997).
 - [23] Y. Iwasa and T. Kaneyasu, *Phys. Rev. B* **51**, 3678 (1995).
 - [24] N. Cegar *et al.*, cond-mat/0002447.
 - [25] Y. Maniwa *et al.*, *Phys. Rev. B* **52**, 7054 (1995); T. Saito *et al.*, *J. Phys. Soc. Jpn.* **64**, 4513 (1995).
 - [26] R. Tycko *et al.*, *Phys. Rev. Lett.* **68**, 1912 (1992).
 - [27] V. Brouet *et al.*, *Phys. Rev. Lett.* **82**, 2131 (1999).
 - [28] J. H. Schon, Ch. Kloc, R. C. Haddon, and B. Batlogg, *Science* **288**, 656 (2000).