Structural Distortion in $Rb_{3-x}C_{60}$ and $K_{3-x}C_{60}$ Revealed by ^{87}Rb- and ^{39}K-NMR

M. Apostol

Universite Montpellier II, GDPC-026, 34095 Montpellier, France

Received: July 27, 1995; In Final Form: October 25, 1995[⊗]

The splitting of the tetrahedral Rb- and K-NMR lines in $Rb_{3-x}C_{60}$ and $K_{3-x}C_{60}$ is analyzed in terms of the mechanism of alkali-cation vacancies. The calculations indicate the presence of vacancies only in the tetrahedral positions, and the interatomic potentials between the alkali cations and the fullerene molecules account satisfactorily for the temperature dependence of the position of the distorted line.

The basic structures of the superconducting fullerides Rb_3C_{60} and K_3C_{60} are well-known.[1−4] The face-centered cubic (fcc) lattice of pure C_{60} is retained, and the Rb or K ions singly occupy the two tetrahedral and one octahedral voids per molecule. Subsequently, detailed profile refinements gave convincing proof that a small but significant concentration of metal vacancies cannot be avoided, even when the global starting composition exceeds three metal ions per C_{60}.[5] This is attributed to an unusually small vacancy formation energy, which has yet to be justified theoretically. The goal of this paper is to examine the consequence of alkali cation vacancies in light of surprising NMR results which indicate the presence of three distinct Rb (or K) sites in the lattice of $Rb_{3-x}C_{60}$ (or, respectively, $K_{3-x}C_{60}$), instead of the two expected for the simple crystallographic structure.[6,7]

Above 450 K the ^{87}Rb-NMR spectrum of $Rb_{3-x}C_{60}$ exhibits two narrow lines, paramagnetically shifted with respect to the reference $^{87}Rb^+$-signal.[6] They originate in the two nonequivalent octahedral (O) and tetrahedral (T) crystalline sites of the Rb-cation, having the intensity ratio 1:2, as expected from the stoichiometry and the (fcc) crystalline structure of this compound. On decreasing the temperature, these lines broaden and move slightly toward smaller shift values; in addition, there appears a third line, denoted T′, whose position evolves rapidly to higher shift values, where it stabilizes around 300 K. At 200 K the shifts are 40 ppm for the O-line, 165 ppm for the T-line, and 270 ppm for the T′-line, and the ratios of their intensities are O:T:T′ = 35:55:10, within an error of ±2.[6] Spin−echo double-resonance experiments[6] showed that the T′-line is a modified T-line, while saturation-transfer experiments[6] and two-dimensional exchange spectroscopy[8] revealed that an exchange appears only between the T- and T′-lines, with a thermally-activated potential barrier of ∼500 meV. Similar results have also been reported for the ^{85}Rb-cation in $Rb_{3-x}C_{60}$,[9] as well as for the ^{39}K-NMR spectrum of $K_{3-x}C_{60}$,[10] except that in the latter case the T−T′ splitting disappears above ∼200 K. We shall discuss herein this T−T′ splitting phenomenon in terms of the recently suggested mechanism of alkali-cation vacancies.[5,7]

The positive shift values of the alkali-cation NMR lines in these compounds indicate the presence of superexchange interaction at the positions of the alkali cations, which means that hyperfine interaction is transferred to a small extent to the s-orbital of the alkali cations. As is well-known, these compounds are ionic compounds to a predominant extent, but the presence of the paramagnetically shifted NMR lines of the
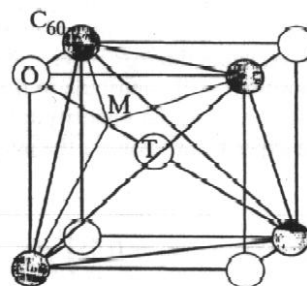
Figure 1. Octahedral (O) and tetrahedral (T) alkali cations in $Rb_{3-x}C_{60}$ and $K_{3-x}C_{60}$, together with the centers of the C_{60}-fullerene molecules; M denotes the center of the equilateral triangle formed by three fullerene molecules.

alkali cations suggest that the outer s-wave electrons of the alkali atoms transferred to the fullerenes still spend a certain time around the nuclei of the alkali cations. It is, therefore, suggested by the NMR data that an alkali cation vacancy is associated with an excess of negative charge, which may originate from the electron left behind the missing alkali cation. The subsequent relaxation of the surrounding environment, the increase in entropy, and the electronic charge transferred from the fullerenes to the neighboring alkali cations will reduce, to a certain extent, the increase in energy and will bring, finally, the compound into a mestastable state, dictated essentially by the process of sample preparation. The key assumption of the vacancy mechanism is that an alkali cation vacancy may change the transferred hyperfine interaction of the surrounding alkali cations via the fullerene molecules; in this way, only those alkali cations which are the nearest neighbors of the fullerene molecules will be affected, i.e. only the tetrahedrally-coordinated alkali cations. The agency role played by the fullerenes in this process is supported by the ionic character of the compounds, as has been said above. The structural unit employed here is the body-centered cube shown in Figure 1, with the side ∼7.1 Å.[3] An alkali-cation vacancy in the octahedral position O in Figure 1 will create an excess of negative charge on the six neighboring fullerene molecules, which, in turn, will increase the hyperfine interaction on their nearest-neighboring alkali cations; these are the eight alkali cations denoted by T in Figure 1, which lie closest to the octahedron formed by the six fullerene molecules. It is assumed that the T′-line originates from these modified tetrahedral positions. Similarly, an alkali-cation vacancy in the tetrahedral site T in Figure 1 will create an excess of electronic charge on the four neighboring fullerene molecules, which, in turn, will increase the hyperfine interaction of their nearest-neighboring alkali cations. It is easy to see that these cations are the six tetrahedral ones facing the edges of the

tetrahedron formed by the four fullerene molecules. These are again tetrahedral positions which are modified by the presence of the vacancy and which are the source of the T'-line. We remark that the extra hyperfine interaction on the modified T-positions, as produced by the presence of the vancancies, explains the position of the T'-line at higher shift values. It is also worth mentioning that the presence of a vacancy will create a local distortion and a small quadrupole coupling as previously remarked,[7,9] the latter being reduced by the decrease in the charge transfer.

According to the picture given above, a vacancy in an octahedral position creates eight modified tetrahedral sites, while a vacancy in a tetrahedral position produces six modified tetrahedral sites. Suppose that in a total of N sites of alkali cations (out of which $\frac{1}{3}N$ are octahedral and $\frac{2}{3}N$ are tetrahedral) we have N_O vacancies in octahedral positions and N_T vacancies in tetrahedral positions, both of them much smaller than N. It follows that the intensity of the O-line will be proportional to $\frac{1}{3}N - N_O$ and that the intensity of the T'-line will be proportional to $8N_O + 6N_T$, while the $\frac{2}{3}N - N_T - 8N_O - 6N_T = \frac{2}{3}N - 8N_O - 7N_T$ positions will contribute to the intensity of the T-line. A least-square fit to the intensity ratios O:T:T' = 35:55:10 given by the experiment[6] requires the minimization of the sum

$$\left(\frac{1}{3} - x_O - 0.35\right)^2 + \left(\frac{2}{3} - 8x_O - 7x_T - 0.55\right)^2 +$$
$$(8x_O + 6x_T - 0.1)^2 \quad (1)$$

where the mole fractions (concentrations) $x_O = N_U/N$ and $x_T = N_T/N$ have been introduced; the sum in eq 1 reads

$$(x_O + 0.02)^2 + (8x_O + 7x_T - 0.11)^2 + (8x_O + 6x_T - 0.1)^2 \quad (2)$$

and one can see easily that eq 2 is minimized for $x_O = -0.2\%$ and $x_T = 1.6\%$; obviously, this means that the physical minimum is reached for $x_O = 0$ and x_T given above. Though the errors in the experimental NMR data used in these calculations are rather large (at least 4%), it is, however, remarkable that these data lead to the present results, which can be viewed as being satisfactorily consistent with the results reported recently from the refined analysis of the X-ray diffraction data of $Rb_{3-x}C_{60}$.[5] Indeed, it has been found in ref 5 that the mole fractions of the alkali-cation vacancies are $x_O \approx 0.7\%$ and $x_T \approx 3.5\%$ within $\pm 1.5\%$. It has been suggested, therefore, that the concentration of the alkali vacancies in the octahedral sites might vanish (or at least be extremely small), and the present calculations based on the NMR data support the same suggestion. We shall assume therefore that the vacancies are placed only in the tetrahedral positions ($x_O = 0$), and their mole fraction is given by $x_T = 1.6\%$. This implies that the stoichiometry of the compound reads $Rb_{2.95}C_{60}$ ($x = 0.05$), the (computational) error in 2.95 being approximately ± 0.01; for an error of 1.5% we have ± 0.05 in ~ 2.9, from the X-ray analysis. As is well-known (see, for example, ref 5), alkali-doped fullerides may also be obtained with a variable content of alkali metals, and their stoichiometry is well assessed both by X-ray and wet-chemistry analysis, though the results of the latter are less reliable for very small values of the vacancy concentrations. An analysis of the T–T' splitting effect, however, is still lacking in these compounds with a variable degree of doping.

We turn now to discussing the temperature effect on the T–T' splitting, as produced by the migration of the vacancies. The overall slight displacement of the O- and T-lines toward lower

shift values on decreasing the temperature (correlated with a similar behavior of the ^{13}C-line) is presumably an effect of the conduction electrons, via an orbital delocalization.[7,10] The broadening of the lines at low temperatures is generally attributed to an increase in the environmental inhomogeneities, correlated with the slowing down of the rotational motion of the fullerene molecules. Here we shall be interested in the evolution with the temperature of the T–T' splitting. It has been shown that the interatomic potentials in the alkali fullerides may be constructed by starting with the (6−12)-Lennard-Jones potential of interaction between an alkali cation and the carbon atoms distributed on the spherical surface of the fullerene molecules.[11,12] Such a potential reads $\epsilon(\sigma^6/2r^{12} - 1/r^6)$, where the parameters are $\epsilon \cong 84.3$ eV Å^6 and $\sigma = 3.58$ Å for Rb and $\epsilon \cong 69.7$ eV Å^6 and $\sigma = 3.46$ Å for K.[11] When the Lennard-Jones contributions of the carbon atoms lying on the spherical surface of the fullerene molecule inside the solid angle under which this molecule is seen from the position of the alkali cation are summed, the potential

$$V(r) = \frac{3\epsilon\sigma^6}{2rR}\left[\frac{1}{(r-R)^{10}} - \frac{1}{(r^2-R^2)^5}\right] =$$
$$\frac{15\epsilon}{2rR}\left[\frac{1}{(r-R)^4} - \frac{1}{(r^2-R^2)^2}\right] \quad (3)$$

is obtained[13] for the interaction of a fullerene molecule with an alkali cation placed at the distance r from its center, R being the radius of the fullerene molecule ($R = 3.5$ Å). These potentials have been used to construct the contributions $V_{T,O}$ of the nearest-neighboring fullerene molecules to the potential energy of the alkali cations in both tetrahedral and, respectively, octahedral coordinations. It has been shown[13] that, in the first approximation, the Coulomb interaction brings only a constant contribution to the energy of the alkali cations around the centers of coordination, as a result of cubic symmetry. The interatomic potential energies $V_{T,O}$ have therefore been used for investigating the equilibrium positions of the alkali cations in the fcc-alkali fullerides,[13] obtaining a consistent picture of both the on-center and the off-center sites for the alkali cations. In addition, it has been shown[13] that the potential given by eq 3 has certain limitations, and some caution should be exercised in dealing with it. First, these potentials (and the corresponding potential energies $V_{T,O}$) are valid around the equilibrium positions of the alkali cations, as the Lennard-Jones parameters are semiempirical quantities derived from data corresponding to such situations. Therefore, the potentials of the type given by eq 3 are not as reliable at very short distances as, for example, those corresponding to an alkali cation close to the surface of a fullerene molecule. Actually, one can estimate the maximum range of validity of these potentials as being that distance over which they vary as much as the absolute magnitude of their minimum values. Secondly, the potential given by eq 3 is an average potential over the carbon atoms assumed uniformly distributed over the spherical surface of teh fullerene molecule; in doing so, we lose the irregularities of the orientational potentials. However, we account for the oriented fullerene molecules, whose hexagons face the alkali cations in the tetrahedral sites, by using an effective radius of the latter $R = 3.5$ Å which is slightly shorter than the average radius ~ 3.65 Å; for such short-range potentials this makes a relatively significant difference. It has also been shown[13] that the second-order expansions of the potential energies around the center of each configuration are given by

$$V_{T,O} = A_{T,O} + B_{T,O}(x^2 + y^2 + z^2) \quad (4)$$

Structural Distortion in $Rb_{3-x}C_{60}$ and $K_{3-x}C_{60}$

J. Phys. Chem., Vol. 100, No. 8, 1996 **3177**

where $A_T = 675$ meV, $B_T = 129$ meV/$Å^2$, $A_O = -624$ meV, and $B_O = 0.6$ meV/$Å^2$ for Rb and $A_T = 139$ meV, $B_T = 83$ meV/$Å^2$, $A_O = -544$ meV, and $B_O = -0.3$ meV/$Å^2$ for K; x, y, and z in eq 4 are the coordinates, measured along the (100)-directions, of a point placed around the center of the octahedral coordination. One can see that the K cations are not stable at the center of the octahedral coordination ($B_O < 0$), acquiring slight off-center sites described by a flat potential.[13] A similar flatness of the potential may also be remarked in the case of the octahedral site of the Rb cation (small values of B_O), although the on-center equilibrium seems to be stable in this case.

Using $B_T = 129$ meV/$Å^2$, we can compute the oscillation frequency $\omega_T = (2B_T/M)^{1/2} = 5.35 \times 10^{12}$ s^{-1} of the Rb cation in the tetrahedral site, where M is the mass of the rubidium atom; it corresponds to a zero-point vibration amplitude ~ 0.08 Å. The jumping rate of the Rb cation from its tetrahedral site is given by

$$k_T = 2.72 \omega_T e^{-\Delta E_T/T} \qquad (5)$$

where T is the temperature, ΔE_T is the potential barrier, and allowance has been made for the thermal average energy. The potential barrier ΔE_T can be estimated from eq 4 by assuming that the tetrahedral cage has an average radius $MT = 7.1/2\sqrt{3}$ Å $= 2.05$ Å, where M is the center of the equilateral triangle formed by three fullerene molecules in Figure 1. We obtain $\Delta E_T \cong 542$ meV, in agreement with the value reported in ref 1 and the analysis of the two-dimensional exchange spectroscopy data.[8] Although the agreement may appear, to some extent, fortuitous, it is, however, worth emphasizing that the analysis of the validity of the estimation presented here suggests that this value should be close to the actual value of the potential barrier.

First, let us remark that the variation ΔE_T found above is comparable with the potential minimum value A_T given below (eq 4); this shows that the quadratic approximation of the potential energy over the distance MT is within the validity range of the potential (eq 3), as discussed above. Secondly, computing the potential energy V_T, as given by eq 3, at the point M, one obtains a much higher value than that given by the quadratic approximation; this energy will even be higher at points situated closer to the surface of the fullerene molecules. However, we should bear in mind that, apart from the fact that the potentials in eq 3 are not adequate at these short distances, as discussed above, the contributions of other fullerene molecules should also be included, as the environment changed at these points; these additional fullerene molecules are placed farther away, so that their attractive contribution will lower the net value of the energy. The tunneling of the alkali cation between two neighboring tetrahedral sites will proceed, most likely, along a curvilinear path passing through the point M. This point, however, defines also the boundary of the tetrahedral cage of the alkali cation. One can see this by comparing the distance between M and the center of the fullerene molecule, which is ~ 5.8 Å, with the sum of the radii of the fullerene molecule, $R = 3.5$ Å; of the Rb cation, $r_{Rb} = 1.49$ Å; and of the C atom lying on the surface of the fullerene. In the case of the C atom we are interested in the extent of its p_z-orbital pointing outward from the fullerene sphere, and since the transferred electrons on the fullerene molecule are shared by many C atoms, we have to look for the extent of this orbital in a neutral C atom. This "radius" r_C of the C atom is then given by $\xi r_C/a_H = Z^* r_C/2a_H \sim 2$, where $a_H = 0.59$ Å is the Bohr radius, Z^* is the effective charge, and $\xi = 1.57$ is known.[14] We obtain $r_C \approx 0.75$ Å (and

remark that it has no connection with the radius 1.7 Å of the chemically-bound carbon) and check that $R + r_{Rb} + r_C \approx 5.75$ Å, i.e. practically the distance given above from the point M to the center of the fullerene molecule. A similar conclusion is reached for the K cation also ($r_K = 1.38$ Å). It follows that the only way for the alkali cations to pass through M is to push away the surrounding fullerene molecules from its path. This slippage of the fullerene molecules will enable the alkali cation to follow its way from M to the similar point in the neighboring tetrahedral configuration, passing through the shared face of the two adjacent cubes somewhere near its center. Since the interatomic potentials vary strongly over short distances and since the tunneling takes place between two identical sites where the harmonic approximation to the potentials holds, it follows that the quadratic approximation to the potentials over the whole cage may be used for estimating the potential barrier, yielding, at least, a lower bound of the actual barrier, in which case the characteristic scale temperature which is given below should be viewed as an underestimate of the actual scale temperature.

Turning now back to estimating the tunneling frequencies, we find that the Rb cation in the octahedral coordination has a much smaller oscillation frequency $\omega_O = 3.6 \times 10^{11}$ s^{-1} and a much higher potential barrier $\Delta E_O > A_T - A_O \cong 1.2$ eV. We conclude that the jumping rate of the Rb cation from the octahedral position is much lower than its jumping rate from the tetrahedral position (by at least 1–2 orders of magnitude), which shows that the vacancies remain in the tetrahedral sites at any temperature, though they are moving among these sites. A similar conclusion is reached for the K cation, whose tetrahedral frequency is $\omega_T = 6.41 \times 10^{12}$ s^{-1} and potential barrier is $\Delta E_T \cong 349$ meV and for which the octahedral jumping rate is vanishingly small.

It is worth mentioning at this point that the vacancy concentration in these alkali-doped fullerides is practically independent of temperature. Two factors concur to this effect. First, the potential barriers produced by the neighboring fullerene molecules (ΔE_T) are high as a consequence of the many contributing carbon atoms on the fullerene surface. Second, the tetrahedral cages are narrow, as shown by the high curvature coefficients B_T in the potential expansion given by eq 4, in contrast with the octahedral sites, and, consequently, the alkali cations in the tetrahedral sites prefer to tunnel through the potential barrier into the neighboring sites rather than to escape out of the sample. As regards the octahedral sites, the height of their potential barrier ΔE_O given above is large enough to prevent both the tunneling (largely diminished by the small values of the coefficients B_O) and the escape. In contrast to other ionic compounds, the alkali-doped fullerides provide deep potential wells for the alkali cations in the narrow tetrahedral sites, which is one of the main reasons for the practically constant vacancy concentration in their case. On the other hand, involving the electronic processes in the mechanism of vacancy formation may also explain the temperature insensitivity of their concentration. The constancy of the vacancy concentration in these compounds over a wide range of temperature, beside being confirmed experimentally by the X-ray analysis,[5] is, in fact, indicated also by the consistency of our analysis given by eqs 1 and 2 of the intensities of the NMR spectrum, which are temperature independent.

At high temperatures the hopping rate of the vacancies given by eq 5 may well exceed the splitting frequency $\Delta \nu_{TT'\mu} \approx 270-165$ ppm; in this case the two exchange-coupled lines (whose intensities are proportional to the vacancy concentration) collapse into a single T'-line. Assuming a factor of 5 for the ratio of the vacancy mobility rate to the splitting frequency $\Delta \nu_{TT'}$

and using the oscillation frequency $\omega_T = 5.35 \times 10^{12}$ s^{-1} and the activation energy $\Delta E_T \simeq 542$ meV derived above for Rb, we obtain a characteristic temperature of ~300 K. At higher temperatures the hopping rate of vacancies given by eq 5, and the corresponding frequency of occurrence of the T–T' splitting, may even overpass the NMR-operating frequency $\nu_{NMR} \simeq 100$ MHz; in the case of Rb this temperature is

$$T^* = \Delta E_T / \ln(6 \times 2.72\omega_T / \nu_{NMR}) = 460 \text{ K} \qquad (6)$$

where the factor 6 has been included in order to account for the six nearest-neighboring T'-sites where a T-vacancy may jump. The temperature given by eq 6 agrees well with the experimentally observed temperature below which the T–T' splitting gradually develops. At $T = 300$ K the hopping rate given by eq 5 is about 10 kHz, indicating that the T–T' splitting is already fully established (with the two exchange-coupled lines collapsed). In the case of K the threshold temperature given by eq 6 is ~290 K, somewhat higher than the experimental value of ~200 K.[10]

There is always an exchange between the T' sites and their neighboring T sites, whose coupling constant κ is modified, at nonvanishing temperatures, by the temperature-dependent k_T given by eq 5 into an effective coupling constant $K = \kappa k_T$ as a result of the vacancy mobility. These exchange-coupled NMR-lines are described by the well-known "Abragam exchange-coupling formula".[15] The remaining T-line may be described by a δ-peak; the number of coupled sites is $N_c = 6N_T$, while the number of remaining T-sites is given by $^2/_3N - 7N_T - N_c = ^2/_3N - 13N_T$. Therefore the intensity formula reads

$$I(\omega) = \left(1 - \frac{39}{2}x_T\right)\delta(\omega - \omega_T) +$$
$$\frac{9x_T}{2\pi} \frac{K(\omega_T - \omega_{T'})^2}{[(\omega - \omega_T)(\omega - \omega_{T'})]^2 + K^2[2\omega - (\omega_T + \omega_{T'})]^2} \qquad (7)$$

At low temperature K is much smaller than $\Delta\omega_{TT'} = \omega_T - \omega_{T'}$, and the two distinct T- and T'-peaks are visible; when the temperature is increased, these two peaks (each of magnitude $9x_T$) collapse into a central peak placed at $^1/_2(\omega_T + \omega_{T'})$. Finally, at high enough temperatures, the T'-line is no longer visible; as we have discussed above, this central peak also disappears, and we are only left with the T-peak. One can check easily that the magnitude of the intensities given by eq 7 is consistent with the value of the vacancy mole fraction x_T obtained above. In addition, the temperature dependence of the two peaks observed experimentally[6,7,9] is also consistent with the description pro-

vided by eq 7. By carefully monitoring the temperature dependence of the positions of the T- and T'-lines, one may extract, by using eq 7, the concentration of vacancies, having thereby another experimental source of assessing this quantity in these compounds. However, as we have said above, a thorough study of the T–T' splitting effect is still lacking, especially in those compounds with a variable content of alkali cations.

In conclusion one may say that the alkali cation vacancies may provide an explanation for the T–T' splitting of the alkali cation NMR-line in $Rb_{3-x}C_{60}$ and $K_{3-x}C_{60}$. The data suggest the presence of the vacancies only in the tetrahedral sites, and their mobility with increasing temperature, as described by the interatomic potentials in the alkali fullerides, gives a satisfactory account of the temperature dependence of the T–T' splitting.

References and Notes

(1) Stephens, P. W.; Mihaly, L.; Whetten, P. L.; Huang, S. M.; Kaner, R. B.; Diederich, F.; Holczer, K. *Nature* 1991, *351*, 632.

(2) Fleming, R. M.; Ramirez, A. P.; Rosseinsky, M. J.; Murphy, D. W.; Haddon, R. C.; Zahurak, S. M.; Makhija, A. V. *Nature* 1991, *352*, 787.

(3) Stephens, P. W.; Mihaly, L.; Wiley, J. B.; Huang, S. M.; Kaner, R. B.; Diederich, F.; Whetten, R. L.; Holczer, K. *Phys. Rev. B* 1992, *45*, 543.

(4) Zhu, Q.; Zhou, O.; Coustel, N.; Vaughan, G.; McCauley, J. P., Jr.; Romanow, W. J.; Fischer, J. E.; Smith, A. B., III. *Science* 1991, *254*, 545.

(5) Fischer, J. E.; Bendele, G.; Dinnebier, R.; Stephens, P. W.; Lin, C. N.; Bykovetz, N.; Zhu, Q. *J. Phys. Chem. Solids* 1995, *56*, 1445.

(6) Walstedt, R. E.; Murphy, D. W.; Rosseinsky, M. *Nature* 1993, *362*, 611.

(7) Zimmer, G.; Helmle, M.; Mehring, M.; Rachdi, F.; Reichenbach, J.; Firlej, L.; Bernier, P. *Europhys. Lett.* 1993, *24*, 59.

(8) Thier, K. F.; Zimmer, G.; Mehring, M.; Rachdi, F.; Fischer, J. E. In *Physics and Chemistry of Fullerenes and Derivatives*; Kuzmany, H., et al. Eds.; World Scientific: Singapore, 1995; p 432.

(9) Yoshinari, Y.; Alloul, H.; Holczer, K.; Foro, L. *Physica* 1994, *C235–240*, 2479.

(10) Alloul, H.; Holczer, K.; Yoshinari, Y.; Klein, O. *Physica* 1994, *C235–240*, 2509.

(11) Mele, E. J. In *Chemical Physics of Intercalation, II*; Bernier, P., et al., Eds.; NATO ASI Series B305; Plenum: New York, 1993; p 93.

(12) Yildirim, T.; Hong, S.; Harris, A. B.; Mele, E. J. *Phys. Rev.* 1993, *B48*, 12262.

(13) Goze, C.; Apostol, M.; Rachdi, F.; Mehring, M. *Phys. Rev.* 1995, *B52*, 1.

(14) Clementi, E.; Raimondi, D. L. *J. Chem. Phys.* 1963, *38*, 2686.

(15) Abragam, A. *Les Principes du Magnetisme Nucleaire*; Presses Universitaires de France: Paris, 1961; p 445.

JP9521666