

**On the structural distortion of the alkali *NMR* spectrum in  $Rb_3C_{60}$  and  $K_3C_{60}$** 

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**Abstract**

The splitting of the tetrahedral *Rb*- and *K*- *NMR* lines in  $Rb_3C_{60}$  and  $K_3C_{60}$  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 inter-atomic potentials between the alkali cations and the fullerene molecules account satisfactorily for the temperature dependence of the position of the distorted line.

Above 450 *K* the  $^{87}Rb$ -*NMR* spectrum in  $Rb_3C_{60}$  exhibits two narrow lines, paramagnetically shifted with respect to the reference  $^{87}Rb^+$ -signal.[1] They originate in the two non-equivalent 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 shift 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  $\pm 2$  .[1] Spin-echo double-resonance experiments[1] showed that the  $T'$ -line is a modified *T*-line, while saturation-transfer experiments[1] and two-dimensional exchange spectroscopy[2] revealed that an exchange appears only between the *T*- and  $T'$ -lines, with a thermally-activated potential barrier of  $\sim 500$  *meV* . Similar results have also been reported for the  $^{85}Rb$ -cation in  $Rb_3C_{60}$ ,[3] as well as for the  $^{39}K$ -*NMR* spectrum in  $K_3C_{60}$ ,[4] except that in the latter case the  $T$ - $T'$  splitting disappears above  $\sim 200$  *K* . We shall discuss herein this  $T$ - $T'$  splitting phenomenon in terms of the mechanism of alkali-cation vacancies.

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 it is well known these compounds are ionic compounds to a predominant extent, but the presence of the paramagnetically shifted *NMR* lines of the 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 a vacancy of alkali cation is accompanied by an excess of negative charge, which may come from the electron left behind the missing cation. The increase in energy resulted in this process is compensated to a various extent by the subsequent relaxation of the neighbouring fullerenes, the corresponding increase in entropy, and the accompanying small transfer of negative charge from the fullerenes to the neighbouring alkali cations. The process brings the compound into a state of local thermodynamical equilibrium (*i.e.* a local minimum of the free energy), which, very probably, might be a metastable 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 on the surrounding alkali cations *via* the fullerene molecules; in this way, only those alkali cations which are the nearest neighbours 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 suggested by the ionic character of the compounds, as it has been said above. The structural unit employed here is the body-centered cube shown in *Fig.1*, with the side  $\sim 7.1 \text{ \AA}$ . [5] An alkali-cation vacancy in the octahedral position  $O$  in *Fig.1* will create an excess of negative charge on the six neighbouring fullerene molecules, which, in turn, will increase the hyperfine interaction on their nearest-neighbouring alkali-cations; these are the eight alkali cations denoted by  $T$  in *Fig.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 *Fig.1* will create an excess of electronic charge on the four neighbouring fullerene molecules, which, in turn, will increase the hyperfine interaction of their nearest-neighbouring 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 vacancies, 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.[3]-[6] the latter being reduced by the decrea

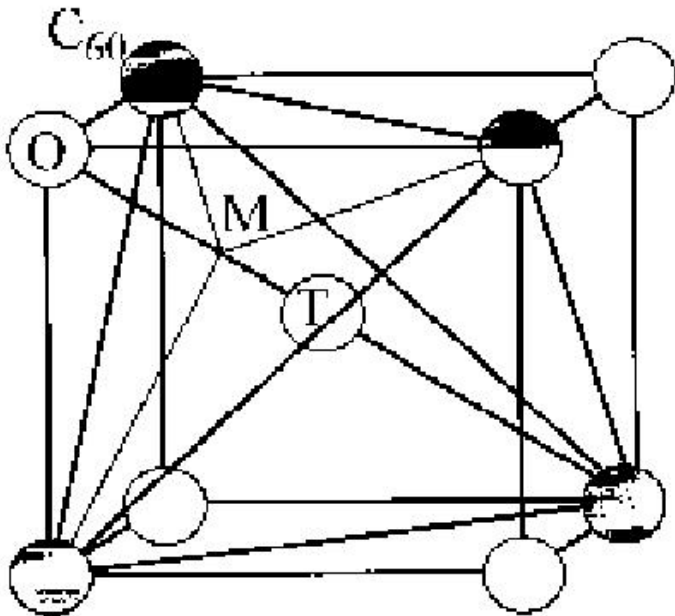


Figure 1: The octahedral ( $O$ ) and tetrahedral ( $T$ ) alkali cations in  $Rb_3C_{60}$  and  $K_3C_{60}$ , together with the centres of the  $C_{60}$ -fullerene molecules;  $M$  denotes the centre of the equilateral triangle formed by three fullerene molecules.

According to the picture given above a vacancy in an octahedral position creates 8 modified tetrahedral sites, while a vacancy in a tetrahedral position produces 6 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  $\frac{1}{3}N - N_O$ , the intensity of the  $T'$ -line will be proportional to  $8N_O + 6N_T$ , while

$\frac{2}{3}N - N_T - 8N_O - 6N_T = \frac{2}{3}N - 8N_O - 7N_T$  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[1] 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 concentrations  $x_O = N_O/N$  and  $x_T = N_T/N$  have been introduced; the sum (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 (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  $Rb_3C_{60}$ . [7] Indeed, it has been found in Ref.7 that the concentrations 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 concentration is given by  $x_T = 1.6\%$ . This implies that the stoichiometry of the compound reads  $Rb_{2.95}C_{60}$ , the (computational) error in 2.95 being  $\sim \pm 0.01$ ; for an error of 1.5% we have  $\pm 0.05$  in  $\sim 2.9$ , from the  $X$ -ray analysis.

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 behaviour of the  $^{13}C$ -line) is presumably an effect of the conduction electrons, via an orbital delocalization. [4] [6] 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 inter-atomic potentials in the alkali fullerenes 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. [8] [9] Such a potential reads  $\varepsilon(\sigma^6/2r^{12} - 1/r^6)$ , where the parameters are  $\varepsilon \cong 84.3 \text{ eV}\text{\AA}^6$ ,  $\sigma = 3.58 \text{ \AA}$  for  $Rb$ , and  $\varepsilon \cong 69.7 \text{ eV}\text{\AA}^6$ ,  $\sigma = 3.46 \text{ \AA}$  for  $K$ . [8] Summing up 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 the potential

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

has been obtained [10] for the interaction of a fullerene molecule with an alkali cation placed at the distance  $r$  from its centre,  $R$  being the radius of the fullerene molecule ( $R = 3.5 \text{ \AA}$ ). These potentials have been used to construct the contributions  $V_{T,O}$  of the nearest-neighbouring fullerene molecules to the potential energy of the alkali cations in both tetrahedral and, respectively, octahedral coordinations. It has been shown [10] that, in the first approximation, the Coulomb interaction brings only a constant contribution to the energy of the alkali cations around the centres of coordinations, as a result of cubic symmetry. The inter-atomic potential energies  $V_{T,O}$  have therefore been used for investigating the equilibrium positions of the alkali cations in the fcc- alkali fullerenes, [10] obtaining a consistent picture of both the on-centre and the off-centre

sites for the alkali cations. In addition, it has been shown[10] that the potential given by (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 semi-empirical quantities derived from data corresponding to such situations. Therefore, the potentials of the type given by (3) are not 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 (3) is an average potential over the carbon atoms assumed uniformly distributed over the spherical surface of the fullerene molecule; 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  $R = 3.5 \text{ \AA}$  which is slightly shorter than the average radius  $\sim 3.65 \text{ \AA}$ ; for such short-range potentials this makes a relatively significant difference. It has also been shown[10] that the second-order expansions of the potential energies around the centre of each configuration are given by

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

where  $A_T = 675 \text{ meV}$ ,  $B_T = 129 \text{ meV/\AA}^2$ ,  $A_O = -624 \text{ meV}$ ,  $B_O = 0.6 \text{ meV/\AA}^2$  for *Rb*, and  $A_T = 139 \text{ meV}$ ,  $B_T = 83 \text{ meV/\AA}^2$ ,  $A_O = -544 \text{ meV}$ ,  $B_O = -0.3 \text{ meV/\AA}^2$  for *K*; one can see that the *K*-cations are not stable at the centre of the octahedral coordination ( $B_O < 0$ ), acquiring slight off-centre sites described by a flat potential.[10] 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-centre equilibrium seems to be stable in this case.

Using  $B_T = 129 \text{ meV/\AA}^2$  we can compute the oscillation frequency  $\omega_T = (2B_T/M)^{\frac{1}{2}} = 5.35 \cdot 10^{12} \text{ s}^{-1}$  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  $\sim 0.08 \text{ \AA}$ . The jumping rate of the *Rb*-cation from its tetrahedral site is given by

$$k_T = 2.72\omega_T e^{-\frac{\Delta E_T}{T}}, \quad (5)$$

where  $T$  is the temperature,  $\Delta E_T$  is the potential barrier, and allowance has been made for the thermal average energy. The potential barrier  $\Delta E_T$  can be estimated from (4) by assuming that the tetrahedral cage has an average radius  $MT = 7.1/2\sqrt{3} \text{ \AA} = 2.05 \text{ \AA}$ , where  $M$  is the centre of the equilateral triangle formed by three fullerene molecules in *Fig.1*. We obtain  $\Delta E_T \cong 542 \text{ meV}$ , in agreement with the value reported in Ref.1 and the analysis of the two-dimensional exchange spectroscopy data.[2] Although the agreement may appear, to a somewhat 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  $\Delta E_T$  found above is comparable with the potential minimum value  $A_T$  given below (4); this shows that the quadratic approximation of the potential energy over the distance  $MT$  is within the validity range of the potential (3), as discussed above. Secondly, computing the potential energy  $V_T$ , as given by (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 fullerenes molecules. However, we should bear in mind that, apart from the fact that the potentials (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 further away, so that their attractive contribution will lower the net value of the energy. However, the potential

near the point  $M$  is still much higher than the potential given by the quadratic approximation. The tunneling of the alkali cation between two neighbouring 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 centre of the fullerene molecule, which is  $\sim 5.8 \text{ \AA}$ , and the sum of the radii of the fullerene molecule  $R = 3.5 \text{ \AA}$ , of the  $Rb$ -cation  $r_{Rb} = 1.49 \text{ \AA}$ , and 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 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 given by  $\xi r_C/a_H = Z^* r_C/2a_H \sim 2$ , where  $a_H = 0.59 \text{ \AA}$  is the Bohr radius,  $Z^*$  is the effective charge and  $\xi = 1.57$  is known.[11] We obtain  $r_C \approx 0.75 \text{ \AA}$  (and remark that it has no connection with the radius  $1.7 \text{ \AA}$  of the chemically-bound carbon), and check that  $R + r_{Rb} + r_C \approx 5.75 \text{ \AA}$ , *i.e.* practically the distance given above of the point  $M$  to the centre of the fullerene molecule. A similar conclusion is reached for the  $K$ -cation also ( $r_K = 1.38 \text{ \AA}$ ). 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 neighbouring tetrahedral configuration, passing through the shared face of the two adjacent cubes somewhere near its centre. One can say that the saddle-point of the potential barrier lies somewhere in this region. While the problem of the tunneling probability of an alkali cation through a deformable three-dimensional potential barrier along curvilinear paths is beyond a simple, direct computation, it lends itself, nevertheless, to a simple, physical approach, which may serve as a guide in discussing the experimental data. Since the inter-atomic potentials vary strongly over short distances, and since the tunneling takes place between two identical sites where the harmonic approximation to the potentials holds, (and since the solid is, of course, not destroyed during this process) 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. This estimation amounts, of course, to assuming that the fullerene molecules and the alkali cations behave as if they were hard spheres as long as the quadratic approximation is trespassed.

Turning now back to estimating the tunneling frequencies, we find that the  $Rb$ -cation in the octahedral coordination has a much smaller oscillation frequency  $\omega_O = 3.6 \cdot 10^{11} \text{ s}^{-1}$ , and a much higher potential barrier  $\Delta E_O > A_T - A_O \cong 1.2 \text{ eV}$ . 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 moving among these sites. A similar conclusion is reached for the  $K$ -cation, whose tetrahedral frequency is  $\omega_T = 6.41 \cdot 10^{12} \text{ s}^{-1}$  and potential barrier  $\Delta E_T \cong 349 \text{ meV}$ , 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 neighbouring fullerene molecules ( $\Delta E_T$ ) are high as a consequence of the many contributing carbon atoms on the fullerene surface. Secondly, the tetrahedral cages are narrow, as shown by the high curvature coefficients  $B_T$  in the potential expansion given by (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 neighbouring sites rather than to escape out of the sample. As regards the octahedral sites, the height of their potential barrier  $\Delta E_O$  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 of a practically constant vacancy concentration in their case. On the other hand, involving the electronic processes in the vacancy formation, as we have said above, may also be another factor in the insensitivity to temperature of the vacancy 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[7], is, in fact, indicated also by the consistency of our analysis given by (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 (5) may well exceed the splitting frequency  $\Delta\nu_{TT'} \approx 270 - 165 \text{ ppm}$ ; in this case the two exchange-coupled lines (whose intensity is proportional with the vacancy concentration) collapse into a single  $T'$ -line; assuming a factor of say, 5 for the ratio of the vacancy mobility rate to the splitting frequency  $\Delta\nu_{TT'}$ , and using the oscillation frequency  $\omega_T = 5.35 \cdot 10^{12} \text{ s}^{-1}$  and the activation energy  $\Delta E_T \cong 542 \text{ meV}$  derived above for *Rb* we obtain a characteristic temperature  $\sim 300 \text{ K}$ . At higher temperatures the hopping rate of vacancies given by (5), and the corresponding frequency of occurrence of the  $T$ - $T'$  splitting, may even overpass the *NMR*-operating frequency  $\nu_{NMR} \cong 100 \text{ MHz}$ ; in the case of *Rb* this temperature is

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

where the factor 6 has been included in order to account for the six nearest-neighbouring  $T'$ -sites where a  $T$ -vacancy may jump. The temperature given by (6) agrees well with the experimentally observed temperature below which the  $T$ - $T'$  splitting gradually develops. At  $T = 300 \text{ K}$  the hopping rate given by (5) is about  $10 \text{ kHz}$ , 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 (6) is  $\sim 290 \text{ K}$ , somewhat higher than the experimental value  $\sim 200 \text{ K}$  [4]

Very likely there is always an exchange between the  $T'$  sites and their neighbouring  $T$  sites, whose small coupling constant  $\kappa$  is modified, at non-vanishing temperatures, by the temperature-dependent  $k_T$  given by (5) into an effective coupling constant  $K = \kappa + k_T$ , as a result of the vacancy mobility. This exchange-coupled *NMR*-lines are described by the well-known "Abragam exchange-coupling formula" [12]. The remaining  $T$ -line may be described by a  $\delta$ -peak; the number of coupled sites is  $N_c = 6N_T$ , while the number of remaining  $T$ -sites is given by  $\frac{2}{3}N - 7N_T - N_c = \frac{2}{3}N - 13N_T$ . Therefore the intensity formula reads

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

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; increasing the temperature these two peaks (each of magnitude  $9x_T$ ) collapse into a central peak placed at  $\frac{1}{2}(\omega_T + \omega_{T'})$ ; 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 (7) is consistent with the value of the vacancy concentration  $x_T$  obtained above. In addition, the temperature dependence of the two peaks observed experimentally[1]·[3]·[6] is also consistent with the description provided by (7). By carefully monitoring the temperature dependence of the positions of the positions of the  $T$ - and  $T'$ -lines one may extract, by using (7), the concentration of vacancies, having thereby another experimental source of assessing this quantity in these compounds.

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  $Rb_3C_{60}$  and  $K_3C_{60}$ . The data suggest the presence of the vacancies only in the tetrahedral sites, and their mobility with increasing temperature, as

described by the inter-atomic potentials in the alkali fullerenes, gives a satisfactory account of the temperature dependence of the  $T-T'$  splitting.

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