# Orientational ordering of $C_{60}$ in the antiferromagnetic $(NH_3)K_3C_{60}$ phase

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The absence of superconductivity in the ammoniated alkali fulleride, $(NH_3)K_3C_{60}$, and the transition to an antiferromagnetic (AF) Mott insulating ground state have been associated with the combined effects of crystal symmetry lowering and increased interfullerene separation. We find that the low-temperature orientational ordering motif of the $C_{60}$ units in the perdeuterated analog, $(ND_3)K_3C_{60}$, correlates well with the three-dimensional AF structure proposed by NMR, which arises through alternate stacking of two-dimensional sheets of $C_{60}$, which order ferrorotationally (antiferromagnetically) along the $\langle 110\rangle$ and antiferrorotationally (ferromagnetically) along the $\langle 1\bar{1}0\rangle$ directions.

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Attempts to drive the superconducting transition temperature $T_c$ of alkali fullerides $A_3C_{60}$ ($A$ = alkali metal) to higher values have focused on synthesizing materials with increased interfullerene separation. However, this has led to electron localization and a transition to an antiferromagnetic (AF) Mott insulating state. The suppression of superconductivity and the metal-insulator transition are thus associated with effects of magnetic origin, providing an important analogy with the phenomenology in organic and high-$T_c$ superconductors.

In particular, introduction of one ammonia molecule in the octahedral site of the fcc structure of $K_3C_{60}$ to form $(NH_3)K_3C_{60}$ led to an anisotropic expansion of the fulleride array, induced a symmetry reduction, and suppressed superconductivity at ambient pressure.[1,2] Muon spin relaxation ($\mu^+$SR) studies provided unambiguous evidence that AF long-range order develops below $T_N \sim 37$ $K$.[3] The temperature evolution of the internal magnetic field below $T_N$ followed closely the behavior of a conventional three-dimensional (3D) Heisenberg AF with $\mu(0) \approx 0.7$ $\mu_B$/molecule. These results were subsequently confirmed by electron spin resonance (ESR) and NMR studies.[4,5] The proximity of $(NH_3)K_3C_{60}$ to a metal-insulator transition can be ascribed to the combined effects of increased interfullerene separation and crystal symmetry lowering. The former leads to a reduced bandwidth $W$ and an increased $(U/W)$ ratio, while the latter lifts the threefold degeneracy of the $t_{1u}$ orbitals and decreases the critical value $(U/W)_c$ (Ref. 6) for the transition to an AF Mott insulating state. Interestingly, recovery of superconductivity with $T_c = 28$ K was reported in $(NH_3)K_3C_{60}$ at pressures $> 1$GPa.[7]

A prominent feature of fullerene-based materials is the sensitivity of their electronic and magnetic properties to orientational order and disorder of the $C_{60}$ units, which gives rise to different relative orientations of the molecular orbitals and different overlap of neighboring electronic wave functions. The relationship between the orientational, orbital, and spin degrees of freedom has been theoretically explored for the $(TDAE)C_{60}$ ferromagnet.[8] The 3D AF structure of $(NH_3)K_3C_{60}$ arises through the alternate stacking along the $c$ axis of 2D AF sheets of $C_{60}$ units which order antiferromagnetically along $\langle 110\rangle$ and ferromagnetically along $\langle 1\bar{1}0\rangle$.[5] It was suggested that this correlates with the antiferroelectric (AFE) ordering of the $K^+-NH_3$ units in the low-temperature (below 150 K) orthorhombic structure of $(NH_3)K_3C_{60}$,[9] which is accompanied by ordering of the $t_{1u}$ molecular orbitals of $C_{60}$. However, as the $C_{60}$ units were assumed to adopt the same orientation in the unit cell, we have attempted to obtain a better understanding of the crystal structure of $(NH_3)K_3C_{60}$ and its implications for the AF order by undertaking a high-resolution powder neutron diffraction study on its perdeuterated analog, $(ND_3)K_3C_{60}$. In this way, we have been successful in determining precisely the $C_{60}$ geometry and orientation together with the location of the ammonia molecules in the pseudo-octahedral holes and their coordination environment. We find that the $C_{60}$ units adopt two distinct orientations related by a 90° rotation about the $c$ orthorhombic axis and are antiferrorotatively ordered along the $a$ and $b$ axes.

$(ND_3)K_3C_{60}$ was prepared by exposing single-phase $K_3C_{60}$ to 0.5 atm of $ND_3$ gas at room temperature for 1 h. After the reaction, the glass tube was sealed under a 0.5 atm partial pressure of $ND_3$ and the sample was annealed at 100°C for 2–3 months. Phase purity was confirmed by powder x-ray diffraction measurements. However, when the powder neutron diffraction measurements were performed, a small amount of unreacted $K_3C_{60}$ was evident, presumably arising during extended storage. The neutron diffraction experiments were undertaken with the high-resolution diffractometer D2b ($\lambda = 1.5944$ Å) at the Institut Laue Langevin, Grenoble, France. The sample, 0.91 g, was loaded in a cylindrical vanadium can (diameter = 5 mm) sealed with indium wire and then placed in a standard ILL "orange" liquid-helium cryostat. The instrument was operated in its high-resolution mode (10′ horizontal primary divergence, 1 cm horizontal monochromator aperture) and the data were collected in the angular range $2\theta = 0° - 164.5°$ in steps of 0.05°. Full diffraction profiles were measured with counting

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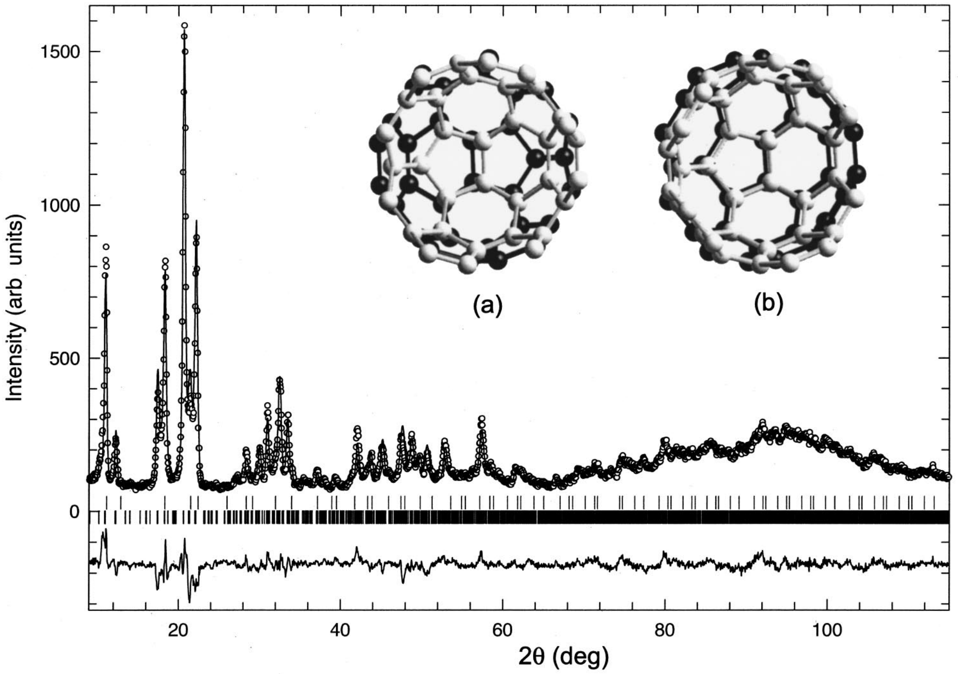

FIG. 1. Final observed (points) and calculated (solid line) neutron ($\lambda = 1.5944$Å) powder diffraction profile for $(\mathrm{ND}_3)\mathrm{K}_3\mathrm{C}_{60}$ at 10 K. The lower panel shows the difference profile and the ticks mark the position of the Bragg reflections of $(\mathrm{ND}_3)\mathrm{K}_3\mathrm{C}_{60}$ (lower) and $\mathrm{K}_3\mathrm{C}_{60}$ (upper). The inset shows the intermolecular $\mathrm{C}_{60}$-$\mathrm{C}_{60}$ nearest contacts, as viewed along the (a) $\langle 110 \rangle$ and (b) ($\langle 1\overline{1}\overline{0} \rangle$) center-to-center directions.

times of 10 h at 10 and 100 K. The raw data were merged, while applying angular and efficiency (vanadium) detector calibrations, using standard ILL programs. The data analysis was performed with the GSAS software.[10] Complementary data were also collected in the temperature range 5–300 K with the medium-resolution high-intensity diffractometer D20 ($\lambda = 2.418$ Å, angular range $= 5°–150°$, step size $= 0.1°$) in an attempt to search for the presence of magnetic order.

Inspection of the high-resolution neutron powder diffraction profile of $(\mathrm{ND}_3)\mathrm{K}_3\mathrm{C}_{60}$ in the $2\theta$ range 9°–115° at 10 K (Fig. 1) shows that almost all Bragg reflections index with the orthorhombic space group $Fddd$. However, refinement of the profile using the LeBail pattern decomposition technique could not account for some reflections, especially in the $2\theta$ range 9–40°. The presence of a minor $\mathrm{K}_3\mathrm{C}_{60}$ impurity was confirmed by a two-phase LeBail profile analysis. Accordingly, the neutron powder diffraction profile was refined by the Rietveld method using a two-phase model of orthorhombic $(\mathrm{ND}_3)\mathrm{K}_3\mathrm{C}_{60}$ and cubic $\mathrm{K}_3\mathrm{C}_{60}$. No evidence for additional Bragg peaks signaling magnetic order was present either in these data or in the low-temperature diffraction profiles collected with the high-intensity D20 diffractometer.

Our starting structural model for the $(\mathrm{ND}_3)\mathrm{K}_3\mathrm{C}_{60}$ phase was based on the orthorhombic structure proposed by Ishii *et al.* (space group $Fddd$).[9] The lattice parameters are obtained by doubling the size of the unit cell of the high-temperature structure ($a = 14.971$Å, $b = 14.895$ Å, $c = 13.687$ Å; space group $Fmmm$).[1] Sixty symmetry-inequivalent carbon atoms are needed to generate the two $\mathrm{C}_{60}$ molecules in the unit cell. These are located at the (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ positions and are oriented in such a way that the three orthogonal twofold axes are aligned with the unit cell vectors and a 6:6 C-C bond of the molecule at the origin aligned parallel to $a$. The pseudotetrahedral potassium atoms are placed in the $8a$, $8b$, $16e$, $16f$, and $16g$ positions, derived from the high-symmetry tetrahedral sites of the $\mathrm{K}_3\mathrm{C}_{60}$ structure, while according to the high-temperature model, the off-centered octahedral $\mathrm{K}^+$ is placed on the $32h$ position $(\frac{1}{4} + \delta x, \delta y, 0)$, where $(\frac{1}{4},0,0)$ is the center of the pseudo-octahedral site and $(\delta x \sim 0.03, \delta y \sim 0.03, 0)$ is the displacement vector. In the x-ray structural model, the $\mathrm{NH}_3$ molecule was approximated by a Ne atom, located in the $32h$ off-centered position, $(\delta x \sim -0.03, \delta y \sim -0.03, 0)$, displaced from the center of the hole in the opposite direction from potassium. In our model, the ammonia molecule is introduced explicitly with the N atom in the original x-ray $32h$ position and the D atoms placed in positions derived from the standard geometry of the $\mathrm{NH}_3$ molecule. The structure of the $\mathrm{K}_3\mathrm{C}_{60}$ minor phase is modeled as cubic (space group $Fm\overline{3}$m).[11]

Our first concern was to determine the exact orientation and geometry of $\mathrm{ND}_3$ in the octahedral void together with its coordination environment to the $\mathrm{C}_{60}$ units. For this reason, we performed a series of Rietveld refinements keeping fixed the geometry of $\mathrm{C}_{60}$ and the positions of the K and N atoms, and allowing only the D atoms to rotate in steps of 5° between 0° and 120° around the $\mathrm{ND}_3$ molecular threefold axis, which is aligned with the $\langle 110 \rangle$ directions.[12] The N-K distance was kept fixed to the x-ray value of 2.57 Å, and the three N-D distances were equal and fixed to 1.00 Å, while all D-N-D angles were equal to 107°. The series of Rietveld refinements was performed in the $2\theta$ range 9–60°, while the lattice constants were kept fixed. The variation of the agreement factor $\chi^2$ of the refinements as a function of the rotation angle $\phi$ showed a well-defined minimum for a clockwise rotation of 35° from the starting orientation. After arriving at this optimum orientation, we checked the $\mathrm{ND}_3$

geometry by varying the D-N-D angle in steps of 1° between 103° and 112°. By following again the evolution of $\chi^2$ as a function of the D-N-D angle, a minimum was found at 109° $(\chi^2=3.55)$.

Despite optimization of the orientation and geometry of the $ND_3$ molecule, the results of the Rietveld refinements in the whole $2\theta$ range were still unsatisfactory, especially at high $2\theta$, as the intensities of numerous reflections were not well reproduced. In general, the high $2\theta$ region of the neutron diffraction profiles of fulleride salts is strongly influenced by the orientational state of the $C_{60}$ units, suggesting that the x-ray structural model of $(ND_3)K_3C_{60}$ may be inadequate in describing correctly the $C_{60}$ orientations. For this reason, a further series of refinements was performed, while allowing the $C_{60}$ molecules to be distributed over two different orientations related by a 90° rotation about the $\langle 001\rangle$ direction. For this model, the two-phase refinement improves significantly $(\chi^2=1.97)$ with the refined values of the fractional occupancies of the C atoms in the two different orientations showing that only 18% of the $C_{60}$ molecules at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ are oriented as in the original x-ray result (orientation I, 6:6 C-C bond parallel to the *b* axis), while 82% adopt orientation II (6:6 C-C bond parallel to the *a* axis). As the changed orientational state of the fulleride units affects the coordination environment of the $ND_3$ molecule in the octahedral voids, its optimal geometry and orientation were reexamined following the same procedure as before. However, the resulting coordination environment of $ND_3$ was now not convincing, as short D-C contacts of 1.89Å were present.

For this reason, we allowed the two orientations of the disordered symmetry-inequivalent $C_{60}$ molecules located at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ to vary independently within the *Fddd* space group. The refinement proceeded smoothly, leading to improved agreement factors with the molecules at (0,0,0) adopting exclusively orientation I, while those at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ adopting exclusively orientation II $(\chi^2=1.90)$, implying antiferrorotative order of the $C_{60}$ units along the three unit cell axes. Although the improvement in the agreement factor was not very large, this was achieved with a smaller number of C positional parameters. In addition, the diffraction profile in the high-$2\theta$ region between 60° and 115° was better accounted for. Further optimization of the geometry and orientation of the ammonia molecule led to a value for the N-K distance of 2.483(7)Å, the N-D distance of 1.00(4)Å, and the D-N-D angle of 108.03(2)°. The coordination environment of the $ND_3$ molecule was checked and no short contacts with C atoms were present. A final Rietveld refinement using the optimized orientation and geometry of the ammonia molecule in the pseudo-octahedral void was then performed and the results are shown in Fig. 1 and Table I. The final values of the lattice constants are $a=29.929(9)$Å, $b=29.787(9)$ Å, and $c=27.136(4)$ Å $(\chi^2=1.62,\ R_{exp}=6.8\%)$. The N-K pair is inclined to the $\langle 110\rangle$ direction at an angle of 3.9°, while all D-C distances assume values greater than 2.4 Å and all K-C contacts are longer than 3.0 Å.

By analyzing the results of the refienements of the three structural models used to describe the orientational state of the fulleride units, the one involving antiferrorotative ordering of the $C_{60}$ units at (0,0,0) and $(\frac{1}{2},0,0)$ (Fig. 2) is the most satisfactory. First, the coordination environment of the $ND_3$ molecule is physically plausible due to the absence of any short D-C contacts and, second, the diffraction profile is much better accounted for in the entire $2\theta$ range and espe-

TABLE I. Final results of the Rietveld refinement of the powder neutron diffraction profile of $(ND_3)K_3C_{60}$ at 10 K (space group *Fddd*, $\chi^2=1.62$, $R_{exp}=6.8\%$). The cell constants are $a=29.929(9)$Å, $b=29.787(9)$Å, and $c=27.136(4)$Å and the weight fraction of the $(ND_3)K_3C_{60}$ phase is 81.8(2)%. The weight fraction of the minority phase $K_3C_{60}$ [space group $Fm\overline{3}m$, $a=14.204(4)$Å] is 18.2(2)%.

| Atom | $x/a$ | $y/b$ | $z/c$ | $B_{iso}/\text{Å}^2$ |
|---|---|---|---|---|
| $C_{60}$(I) | 0 | 0 | 0 | 3.2(2) |
| $C_{60}$(II) | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | 3.2(2) |
| K(1) | $\frac{1}{8}$ | $\frac{1}{8}$ | $\frac{1}{8}$ | 1.9(2) |
| K(2) | $\frac{1}{8}$ | $\frac{1}{8}$ | $\frac{5}{8}$ | 1.9(2) |
| K(3) | $\frac{3}{8}$ | $\frac{1}{8}$ | $\frac{1}{8}$ | 1.9(2) |
| K(4) | $\frac{1}{8}$ | $\frac{3}{8}$ | $\frac{1}{8}$ | 1.9(2) |
| K(5) | $\frac{1}{8}$ | $\frac{1}{8}$ | $\frac{3}{8}$ | 1.9(2) |
| K(6) | 0.285 | 0.032 | 0 | 5.6(2) |
| N(1) | 0.2222(6) | 0.9776(6) | -0.0002(5) | 5.6(2) |
| D(1) | 0.217(2) | 0.963(2) | 0.033(2) | 5.3(2) |
| D(2) | 0.195(2) | 0.996(2) | -0.009(1) | 5.3(2) |
| D(3) | 0.225(2) | 0.953(2) | -0.025(2) | 5.3(2) |

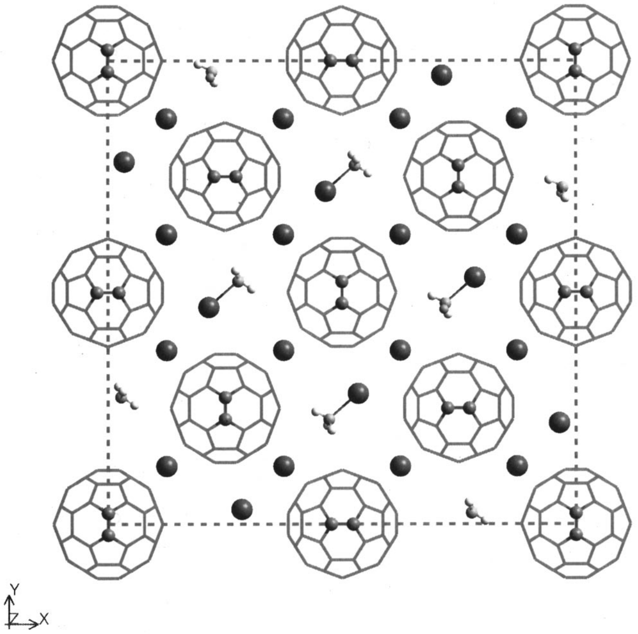

FIG. 2. Projection of the face-centered orthorhombic structure of $(ND_3)K_3C_{60}$ on the [110] basal plane. The ferrorotative (antiferrorotative) order of $C_{60}$ along the base diagonal $\langle 110\rangle$ $(\langle 1\overline{1}0\rangle)$ is shown.

cially at high angles which is crucial in defining the orientational state of the $C_{60}$ units. Finally it is of interest to note that the geometry that the $ND_3$ molecule adopts when coordinated to $K^+$ in the octahedral site and surrounded by six $C_{60}$ units is quite similar to that in the gas phase. The D-N-D angle has increased somewhat to 108°. This is expected, as the bonding interaction between N and $K^+$ should result in an opening of the D-N-D angle.

A neutron diffraction profile of $(ND_3)K_3C_{60}$ was also collected at 100 K. No evidence of any phase change was present and two-phase Rietveld refinement of the data proceeded smoothly, leading to orthorhombic lattice constants $a = 29.923(18)$ Å, $b = 29.831(17)$ Å, and $c = 27.180(4)$ Å ($\chi^2 = 1.65$, $R_{exp} = 7.2\%$).

The neutron powder diffraction measurements employed in this work to derive the low-temperature crystal structure of $(ND_3)K_3C_{60}$ have revealed a superstructure arising from a unique orientational ordering motif of the $C_{60}$ units within the unit cell (Fig. 2). In general, the crystal structures of fulleride salts can be classified into those comprising orientationally disordered and orientationally ordered $C_{60}$ units. The former include systems with merohedral [$K_3C_{60}$(Ref. 11)], orientational [$Na_2CsC_{60}$ (Ref. 13)], or quasispherical [$Li_2CsC_{60}$ (Ref. 14)] disorder of the fulleride ions. The latter are typified by the bcc-based $K_6C_6$0 salt[15] in which all units adopt the same orientation and $Ba_3C_{60}$ in which the molecule at the center of the unit cell is rotated by 90° with respect to that at the origin.[16] An ordered superstructure of $K_3C_{60}$ in which the $C_{60}$ orientation alternates from one (001) plane to the next (space group $P4_2/mnm$) has been discussed theoretically[17] but has not been observed experimentally.

The observed orientational ordering pattern in $(ND_3)K_3C_{60}$ is that of 2D sheets of $C_{60}$ which order ferrorotationally (orientation I) along the $\langle 110 \rangle$ and antiferrorotationally (orientations I and II) along the $\langle 1\bar{1}0 \rangle$ directions and which stack alternately along the $c$ axis. There is a remarkable correlation of this superstructure with the 3D AF structure derived from NMR experiments and the proposed molecular orbital scheme[5] (Fig. 3). In the latter, the $C_{60}$ units along [110] order antiferromagnetically, while those along $[1\bar{1}0]$ ferromagnetically. This implies that the nature of the intermolecular magnetic exchange interactions sensitively depends on the relative orientation of near-neighbor $C_{60}$ units. Figure 1 (inset) shows the nearest contacts between $C_{60}$ along [110] and $[1\bar{1}0]$. In both cases, 6:5 C-C bonds face each other when viewed along the center-to-center direction but the existence of a center of inversion along [110] leads to pentagonal faces directed over hexagons and vice versa. In contrast, along $[1\bar{1}0]$ pentagonal (hexagonal) faces of near neighbors align over pentagons (hexagons). The observed ordering pattern is reminiscent of that proposed theoretically to account for the development of ferromagnetism in $(TDAE)C_{60}$.[8]

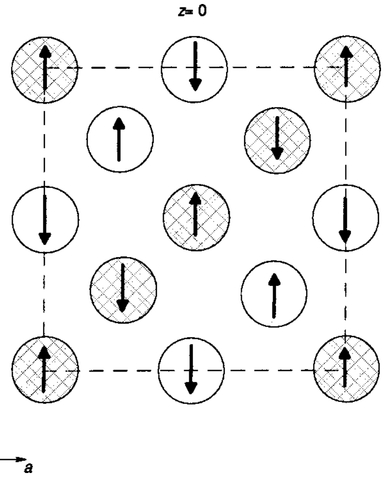

FIG. 3. Schematic diagram of orientational and magnetic order in the basal plane of the $(ND_3)K_3C_{60}$ structure. Shaded (open) circles denote orientation I (II) of $C_{60}$. The moment directions have yet to be determined and have been arbitrarily placed parallel to the $b$ axis.

In conclusion, we have identified in $(ND_3)K_3C_{60}$ a unique ordering pattern of the $C_{60}$ units in the unit cell and shown that the $C_{60}$ orientational degrees of freedom play an active role in the electronic and magnetic response of $(ND_3)K_3C_{60}$. The orientational ordering motif gives rise to distinct orbital ordering which modulates the intermolecular exchange interactions. The experimental observation that the orientational ordering temperature is higher than $T_N$ suggests that the former is the driving force.

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[1] M.J. Rosseinsky *et al.*, Nature (London) **364**, 425 (1993).
[2] Y. Iwasa *et al.*, Phys. Rev. B **53**, R8836 (1996); K.M. Allen *et al.*, J. Mater. Chem. **6**, 1445 (1996).
[3] K. Prassides *et al.*, J. Am. Chem. Soc. **121**, 11 227 (1999).
[4] F. Simon *et al.*, Phys. Rev. B **61**, R3826 (2000).
[5] H. Tou *et al.*, Phys. Rev. B **62**, R775 (2000).
[6] E. Koch *et al.*, Phys. Rev. Lett. **83**, 620 (1999).
[7] O. Zhou *et al.*, Phys. Rev. B **52**, 483 (1995).
[8] K. Tanaka *et al.*, Chem. Phys. Lett. **259**, 574 (1996); T. Kawamoto, Solid State Commun. **101**, 231 (1997).
[9] K. Ishii *et al.*, Phys. Rev. B **59**, 3956 (1999).
[10] A. C. Larsen and R. B. von Dreele, Computer code GSAS, Los Alamos National Laboratory, 1986.
[11] P.W. Stephens *et al.*, Nature (London) **351**, 632 (1991).
[12] The starting geometry of the $ND_3$ molecule was N(1) (0.220,0.975,0), D(1) (0.191,0.989,0.011), D(2) (0.215,0.962,-0.034), and D(3) (0.226,0.949,0.023).
[13] K. Prassides *et al.*, Science **263**, 950 (1994).
[14] I. Hirosawa *et al.*, Science **264**, 1294 (1994).
[15] O. Zhou *et al.*, Nature (London) **351**, 462 (1991).
[16] A.R. Kortan *et al.*, Phys. Rev. B **47**, 13 070 (1993).
[17] S. Satpathy *et al.*, Phys. Rev. B **46**, 1773 (1992).