

Solid-state ^{23}Na and ^{13}C NMR characterization of Na_3C_{60}

Robert W. Schurko,* Mathew J. Willans, Boris Skadtchenko, and David M. Antonelli

Department of Chemistry and Biochemistry, University of Windsor, 401 Sunset Ave. Windsor, Ont., Canada, N9B 3P4

Received 20 October 2003; received in revised form 5 February 2004; accepted 13 February 2004

Abstract

Two separate samples of Na_3C_{60} were prepared by direct reaction of C_{60} with sodium metal vapor, and subjected to different annealing times of 10 days and 16 days. Solid-state ^{13}C and ^{23}Na NMR, along with elemental analysis, powder X-ray diffraction (XRD) and Raman spectroscopy, were used to characterize both samples. The Raman spectra of both materials have a single peak at 1447 cm^{-1} which correspond to the A_g peak of C_{60}^{3-} , consistent with the stoichiometry of Na_xC_{60} with $x = 3$. The powder XRD patterns are also virtually identical for both samples. However, solid-state ^{23}Na and ^{13}C NMR spectra of the two samples are significantly different, suggesting a relationship between annealing times and the final structure of the alkali fulleride. Variable-temperature ^{23}Na magic-angle spinning (MAS) NMR experiments reveal the existence of two or three distinct sodium species and reversible temperature-dependent diffusion of sodium ions between octahedral and tetrahedral interstitial sites. ^{13}C MAS NMR experiments are used to identify resonances corresponding to free C_{60} and fulleride species, implying that the samples are segregated-phase materials composed of C_{60} and non-stoichiometric Na_3C_{60} . Variable-temperature ^{13}C MAS NMR experiments reveal temperature-dependent motion of the fullerenes.

© 2004 Elsevier Inc. All rights reserved.

Keywords: Solid-state NMR; ^{23}Na NMR; Fullerenes; Fullerides; Solid-state chemistry

1. Introduction

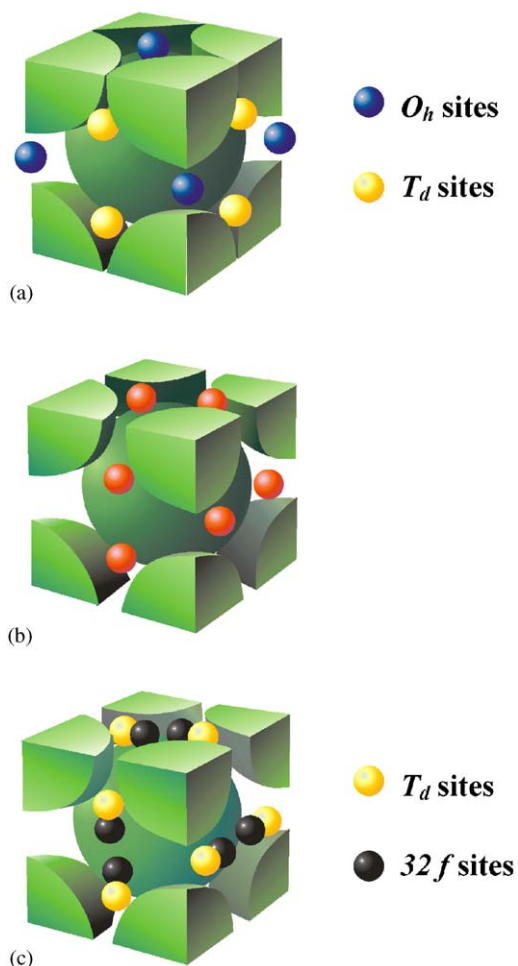
More than a decade after the discovery of fullerene (C_{60}) [1], the solid-state structures and electronic properties of fullerene materials continue to be an area of great interest. Of particular importance are the alkali fullerides [2,3], which have molecular formulae $[A]_x^+[\text{C}_{60}]^{x-}$, where $A = \text{Li, Na, K, Rb or Cs}$ and $x = 1-6$. Depending upon the preparation method and the relative amount of alkali metal and fulleride, the C_{60}^{x-} anion can have a variety of oxidation states. The presence of one or more oxidation states in samples with a mean stoichiometry of $A_3\text{C}_{60}$ ($A = \text{K, Rb, Cs}$) has been invoked as an explanation for metallic and superconducting behavior in these materials [4,5], which by most calculations should be Mott-Hubbard insulators, though this is the subject of some debate [6]. The so-called “hole-doped Mott-Hubbard insulator” model has also been used to help understand superconductivity in these materials [5]. Pristine C_{60} is known to have an *fcc* (face-centered cubic) structure at room temperature,

whereas the alkali fullerides can have *fcc*, *bct* (body-centered tetragonal) or *bcc* (body-centered cubic) lattices, depending upon both the stoichiometric ratio of A to C_{60} and the ionic radius of the alkali metal atom [5,7]. Alkali metal atoms occupy sites of octahedral or tetrahedral symmetry (Scheme 1a), and the latter sites are smaller than the former in $A_3\text{C}_{60}$ alkali fullerides [8,9]. However, for Na_3C_{60} and numerous other alkali fullerides, there is controversy with regard to the actual positions of the cations, and in some cases, the number of alkali metal atoms at these sites [10–12]. Occupation of the tetrahedral site with ions larger than Na results in an increase in the dimensions of the unit cell (“lattice expanding”), and occupation of the octahedral site with any type of cation decreases these dimensions (“lattice contracting”) [10]. Sodium fullerides are significantly different from their K, Rb and Cs counterparts, in terms of both their molecular structure and bulk physical properties [13]. Most notably, Na_3C_{60} is not superconducting at any temperature above 2.5 K [10], which is thought to arise from the instability of the *fcc* lattice at low temperatures [14]. As well, the preparation of bulk phase Na_3C_{60} is non-trivial and is often exists as a segregated mixture of C_{60} and Na_3C_{60} [12].

*Corresponding author. Fax: +519-973-7098.

E-mail address: rschurko@uwindsor.ca (R.W. Schurko).

URL: <http://www.uwindsor.ca/schurko>.



Scheme 1. Graphical illustration of: (a) Na_3C_{60} *fcc* structure with octahedral and tetrahedral sites, (b) the hypothetical "A15" structure of A_3C_{60} with generalized low symmetry positions, and (c) *fcc* structure showing migration of sodium ions in tetrahedral sites to generalized positions.

Solid-state nuclear magnetic resonance has been a key method of characterization for fullerenes and fullerides. Specifically, solid-state ^{13}C NMR is one of the most important probes of structure in both pure fullerite and alkali fullerides [7,13], finding use in many instances to distinguish between fullerene [15] and fulleride species [16–19], as well as to examine the molecular dynamics of C_{60} [20]. Solid-state NMR experiments on half-integer quadrupolar nuclei (i.e., nuclear spin $I = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$) have more recently come to the forefront as a method of characterizing molecular structure and dynamics in inorganic and organic materials [21–23]. Since all of the alkali metals from Li to Cs have half-integer quadrupolar nuclear isotopes which are useful from the NMR standpoint, numerous experiments have been conducted on alkali fullerides, including ^7Li NMR of Li_xC_{60} [24], ^{39}K NMR of K_3C_{60} [25], and $^{85/87}\text{Rb}$ and ^{133}Cs NMR studies of Rb_3C_{60} and $\text{RbCs}_2\text{C}_{60}$ [26].

The unusual shapes of the powder patterns that appear in solid-state NMR spectra of half-integer quadrupolar nuclei result from the quadrupolar interaction, which is the interaction of the electric quadrupole moment of the nucleus with large electric field gradients (EFGs) within the molecule. The EFGs are described by a traceless symmetric second-rank tensor \mathbf{V} , which has principal components in its own principal axis system which are defined such that $|V_{33}| \geq |V_{22}| \geq |V_{11}|$. The magnitude of the quadrupolar interaction is given by the nuclear quadrupolar coupling constant, C_Q , which is defined as $C_Q(\text{MHz}) = eQV_{33}/h$, where Q is the nuclear quadrupole moment. The axial symmetry of the quadrupolar interaction is expressed by the unitless quadrupolar asymmetry parameter, η_Q , which is defined as $\eta_Q = (V_{11} - V_{22})/V_{33}$. The quadrupolar interaction can be utilized as a probe of the spherical (C_Q) and axial (η_Q) symmetry of the ground-state electronic environment about a nucleus. Further discussion of the quadrupolar interaction is beyond the scope of this article and the reader is referred to a number of excellent review articles on NMR of quadrupolar nuclei [22,27,28].

Solid-state ^{23}Na NMR experiments have been reported for a variety of alkali fullerides, and have been utilized to distinguish between the tetrahedral and octahedral sodium sites, as well as to observe temperature-dependent chemical exchange processes. For instance, static ^{23}Na NMR experiments on Na_2C_{60} and Na_6C_{60} revealed a powder pattern with a center of gravity at 73 ppm for the former (corresponding to a single tetrahedral sodium site) and two separate powder patterns centered at 73 and 147 ppm for the latter (corresponding to the presence of both single tetrahedral sites and octahedral sodium tetramers) [29]. ^{23}Na NMR resonances in these samples are shifted to high frequency due to "the presence of residual charge on the Na ions". NMR experiments conducted upon Na_6C_{60} while heating between 300 and 400 K under vacuum reveal a single resonance at 120 ppm, corresponding to rapid chemical exchange of the sodium ions between the tetrahedral and octahedral sites. Variable-temperature ^{23}Na NMR experiments on NaC_{60} revealed that at ambient or low temperatures, the tetrahedral sodium sites are disordered and increasing temperature results in an increase in symmetry about the sodium ions, which is attributed to movement of Na^+ ions into "on-center" tetrahedral positions [30]. The ^{23}Na NMR powder patterns are also shifted to high frequency at ambient temperatures for these complexes. NMR studies on $\text{Na}_2\text{CsC}_{60}$ and $\text{Na}_2\text{RbC}_{60}$ have also been reported, where individual paramagnetically shifted sodium resonances have been resolved [31,32]. ^{23}Na NMR spectra of the "crowded" *fcc* $\text{Na}_{9.7}\text{C}_{60}$ fulleride reveal three types of sodium environments, some of which contain clusters of sodium atoms [14].

Na_3C_{60} has been the focus of much experimental investigation due to its stoichiometric and structural similarity to K_3C_{60} , but lack of superconductivity at high temperatures [10,12,14,33]. The refined powder X-ray diffraction (XRD) structure for Na_3C_{60} indicates a room-temperature *fcc* structure with Na sites of both octahedral and tetrahedral symmetry, though a great deal of positional disorder is suggested for the octahedral sites [12]. Additional powder XRD and NMR studies on Na_3C_{60} suggest that the sodium ions may be displaced into a general position (32*f*) as opposed to two separate sites, perhaps in an arrangement similar to the *A15* structure of Rb_3C_{60} [10,12]. In this same paper, application of ^{23}Na NMR to examine the alkali sites in a series of fullerenes is mentioned, though no description of experimental ^{23}Na NMR data is provided. Both powder XRD studies report a reversible structural phase transition between 250 and 260 K, which is attributed to either a macroscopic phase transition or migration of sodium ions between sites of different crystallographic symmetry [10,12]. Bulychev and co-workers have made an attempt to study Na_3C_{60} and Na_6C_{60} by solid-state ^{23}Na NMR (vide infra) [34].

Our own particular interest in the bulk phase Na_3C_{60} samples was spurred on by recent work in our research groups on the synthesis and structural characterization of composite materials produced by loading mesoporous transition metal oxides with alkali fullerenes [35]. Solid-state NMR experiments on these mesoporous materials revealed a great variety of structural types and fullerene species which were highly dependent upon the degree of reduction of the framework metal oxide. Herein, we report a comprehensive solid-state ^{23}Na and ^{13}C NMR, powder X-ray diffraction and Raman spectroscopic study of two separately prepared samples of bulk phase Na_3C_{60} (at various stages of annealing) in an effort to shed further light upon its structure and the effects of annealing times on the stoichiometry and purity of the samples. ^{23}Na magic-angle spinning (MAS) NMR is used to identify different sodium environments within the samples, and to observe migration of sodium ions between interstitial sites of different symmetry. ^{13}C NMR is used to distinguish different fullerene and fullerene species, and to assess the homogeneity and composition of the samples. Variable-temperature NMR experiments are used to examine temperature-dependent structural changes and the unique species that arise within certain temperature regimes.

2. Experimental

2.1. Materials and equipment

All chemicals, unless otherwise stated, were obtained from Aldrich and used without further purification.

Na_3C_{60} was synthesized by heating C_{60} and Na together in a sealed tube between 400°C and 450°C for 10 days (sample A) and 16 days (sample B) [36]. Both samples were sealed in glass capillary tubes under an inert atmosphere and characterized by powder XRD [8]. XRD powder patterns were obtained on a Siemens D-500 X-ray diffractometer with a $\text{CuK}\alpha$ source. Raman spectra were recorded on a Renishaw Ramascope using a Renishaw 514 nm Diode Laser System.

Solid-state ^{23}Na and ^{13}C NMR spectra were obtained on a Varian Infinity Plus NMR spectrometer with a 9.4 T (400 MHz) Oxford wide-bore magnet ($\nu_0(^{23}\text{Na}) = 105.74$ MHz, $\nu_0(^{13}\text{C}) = 100.63$ MHz). A Varian/Chemagnetics 4 mm double-resonance MAS probe and a Varian/Chemagnetics 4 mm triple-resonance MAS probe (operating in double-resonance ^1H - ^{23}Na or ^1H - ^{13}C configurations) were used for all experiments. Samples were ground into fine powders under an atmosphere of dry nitrogen and tightly packed into 4 mm o.d. zirconium oxide rotors, which were sealed with air-tight Teflon spacers. Sodium chemical shifts were referenced to a 1.0 M solution of NaCl ($\delta_{\text{iso}}(^{23}\text{Na}) = 0.0$ ppm). ^{23}Na MAS NMR spectra were obtained using rotor-synchronized Hahn-echo ($\pi/2 - \tau - \pi - \tau - \text{acq}$) experiments, with a spinning speed of $\nu_{\text{rot}} = 12$ kHz and interpulse delays of $\tau = 1/\nu_{\text{rot}} = 83.3$ μs (standard ^{23}Na MAS Bloch decay experiments resulted in missing points at the beginning of the FID, which lead to distorted baselines and phasing difficulties after Fourier transform). Typical experimental parameters for the ^{23}Na experiments include an RF field amplitude of $\nu_1 = 33.3$ kHz, a central-transition selective pulse width of 3.5 μs and calibrated recycle delays ranging from 1 to 7 s. The number of scans acquired for room-temperature ^{23}Na MAS NMR spectra of Na_3C_{60} was 2576, whereas variable-temperature ^{23}Na NMR experiments involved the collection of 208 scans, over a temperature range of -120°C to 200°C (temperatures reported herein are accurate to within $\pm 2^\circ\text{C}$, based on temperature calibrations). Solid-state ^{13}C MAS NMR spectra were referenced to TMS ($\delta_{\text{iso}}(^{13}\text{C}) = 0.0$ ppm) by setting the high frequency resonance of solid adamantane to 38.57 ppm. Single-pulse experiments were conducted on all samples, with a spinning rate of $\nu_{\text{rot}} = 12$ kHz. An RF field of $\nu_1 = 125$ kHz, a $\pi/2$ pulse width of 1.95 μs and recycle delays of 8 or 9 s were employed in all ^{13}C NMR experiments. Variable-temperature ^{13}C MAS NMR experiments were performed from -120°C to 200°C with the same parameters as the room-temperature spectra, except that the spinning speed and the number of transients collected were decreased to 10 kHz and 100 scans, respectively.

Analytical simulations of the ^{23}Na NMR spectra were performed on a Pentium III computer using the WSOLIDS simulation package (developed by K.

Eichele and R.E. Wasylishen at Dalhousie University). Elemental analysis was conducted under an inert atmosphere by Guelph Chemical Laboratories, Ltd., 248 Silvercreek Pkwy, N. Guelph, Ont., Canada, N1H 1E7. Vanadium pentoxide was added to the samples to ensure complete carbon combustion.

3. Results and discussion

3.1. Preparation of samples and characterization by Raman spectroscopy, powder XRD and elemental analysis

Samples of Na_3C_{60} were prepared by annealing a stoichiometric mixture of Na metal and C_{60} in a vacuum-sealed tube between 400°C and 450°C for 10 days (A) and 16 days (B). After 10 days there was no metallic sodium visible in the reaction mixture for both samples. The XRD patterns of the two samples are virtually identical, displaying the expected [111], [200] and [220] reflections at lower angles (Fig. 1). Raman spectra of both samples are shown in Fig. 2, each possessing a single fulleride A_g band at 1447 cm^{-1} , which is consistent with the presence of C_{60}^{3-} fullerides and a fulleride stoichiometry of Na_xC_{60} of $x = 3$. The elemental analysis yields carbon percentages of 91.50% and 92.67% for samples A and B, respectively (actual elemental composition: C 91.27%, Na 8.73%).

3.2. A previous solid-state NMR study of Na_3C_{60}

Before discussing our own data, it is prudent to first consider the work of Bulychev and co-workers, who examined the solid alkali-metal fullerides Na_3C_{60} and Na_6C_{60} with solid-state ^{23}Na , ^{13}C and ^1H NMR experiments [34]. NMR data were obtained for both

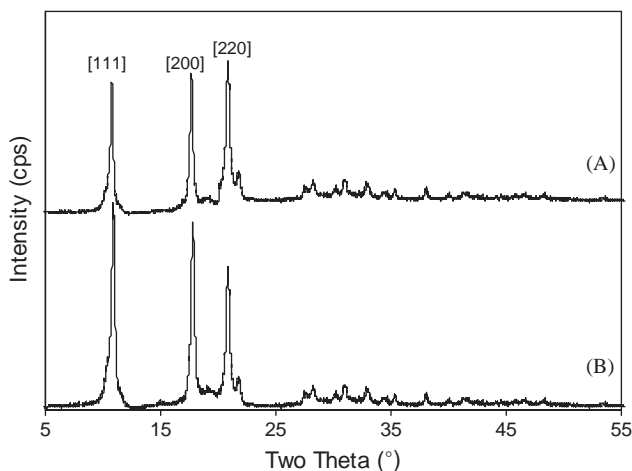


Fig. 1. XRD pattern of Na_3C_{60} annealed for: (A) 10 days and (B) 16 days.

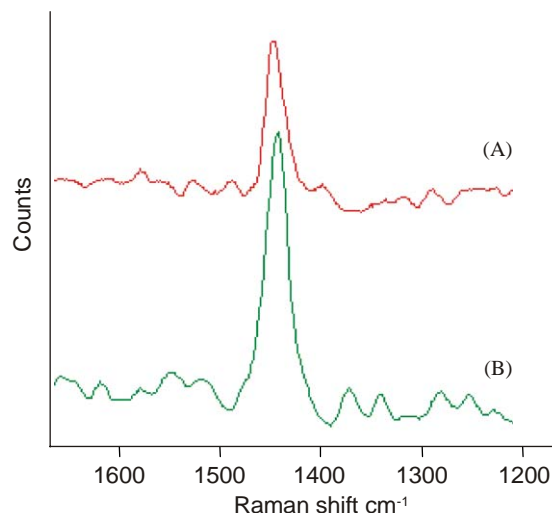


Fig. 2. Raman A_g band of Na_3C_{60} samples (A) and (B). The peak centered at 1447 cm^{-1} corresponds to C_{60}^{3-} .

Na_3C_{60} and Na_6C_{60} at various stages of synthesis: (i) immediately after discoloration of the toluene solution (multi-phased precipitate), (ii) after annealing at 400 K for 10–15 days, and (iii) after drying the annealed samples between 600 and 620 K. A peak at 1133 ppm, indicative of unreacted Na metal, is observed for both samples in stage (i). ^{23}Na NMR spectra of Na_3C_{60} after a short annealing period reveal two powder patterns centered at 290 and 215 ppm, and then after drying at 78 and 26 ppm. The powder patterns at 78 and 26 ppm likely correspond to octahedral and tetrahedral sites, respectively, in accordance with work by Rachdi and co-workers on Na_2C_{60} and Na_6C_{60} [29]. However, the sodium resonances of Na_3C_{60} are not paramagnetically shifted as in the case of Na_2C_{60} and Na_6C_{60} . Corresponding ^{13}C NMR experiments reveal a single broad powder pattern initially centered at 203 ppm, which shifts to 189 ppm after annealing, and then further to 181 ppm after drying at 600 K. Unfortunately, no ^{23}Na or ^{13}C NMR spectra acquired under conditions of MAS are presented, and the exact isotropic chemical shifts (as well as contributions from the quadrupolar interaction in the case of ^{23}Na) are impossible to ascertain from these powder patterns. The NMR data for Na_6C_{60} is less conclusive, as experiments conducted on the same sample yield ^{23}Na NMR spectra of variable appearance. Nonetheless, for both Na_3C_{60} and Na_6C_{60} , Bulychev et al. point out that the synthesis of alkali fullerides in the presence of a solvent phase is promising but non-trivial, since (i) sodium atoms slowly intercalate into the fulleride lattice; (ii) solvent choice may influence synthesis of the fullerides; and (iii) the dynamic behavior of the sodium atoms in the solid lattice is very intricate and still not well understood.

3.3. ^{23}Na MAS NMR of Na_3C_{60}

Variable-temperature ^{23}Na MAS NMR spectra acquired from -120°C to 200°C are shown in Figs. 3A and B for Na_3C_{60} (A) and Na_3C_{60} (B), respectively, and comparison of experimental and simulated spectra for both samples at selected temperatures are shown in Figs. 4A and B. The spectra of B, the sample that underwent the longer annealing period, are somewhat more simple to interpret than those of A and shall be discussed first. In the ^{23}Na MAS NMR spectrum of Na_3C_{60} (B) at 200°C , there is a broad powder pattern affected by a significant second-order quadrupolar interaction, which can be simulated (Fig. 4B) to yield the quadrupolar parameters $C_Q(^{23}\text{Na}) = 3.3(2)$ MHz and $\eta_Q = 0.08(2)$, as well as the isotropic chemical shift, $\delta_{\text{iso}}(^{23}\text{Na}) = +17.2(5)$ ppm. As the temperature is decreased, the pattern broadens and the C_Q is observed to gradually increase (increases in C_Q at low temperatures typically result from reduced motional averaging of the principal components of the EFG tensor due to attenuated molecular motion) [37]. Broad, low-intensity, high-frequency resonances, which may arise from the presence of paramagnetic fulleride species, shift from $+95$ to $+80$ ppm between 100°C and 200°C . These resonances disappear at 50°C and do not reappear at lower temperatures. No high frequency resonances in the vicinity of $+1100$ ppm are observed, indicating that there is no unreacted sodium metal present in these samples [34]. At room temperature, $C_Q(^{23}\text{Na}) = 3.55(6)$ MHz, $\eta_Q = 0.08(2)$ and $\delta_{\text{iso}}(^{23}\text{Na}) = +17.4(5)$ ppm. The close agreement between simulations and experimental data, coupled with the observation of decreasing values of C_Q with

increasing temperature, suggest a single type of sodium environment at room temperature and above, rather than separate tetrahedral and octahedral sites [12]. The powder pattern is slightly broadened, which may suggest long-range disorder or clustered arrangements of sodium ions.

As the temperature is dropped to -30°C , a second sharp resonance becomes evident (Fig. 3B). This resonance is influenced by a small quadrupolar interaction (no second-order lineshape or sharp spinning sidebands are visible) and has a center of gravity that moves gradually from -15.0 ppm at -30°C to -17.2 ppm at -120°C . The temperature at which this resonance appears corresponds with a “symmetry-decreasing” phase transition observed by powder XRD at ca. -23°C [10]. The authors of this work suggest that this transition occurs either as the result of migration of sodium ions from octahedral to tetrahedral sites or the disproportionation of a single phase with sodium ions in generalized $32f$ positions (Scheme 1b) into two fcc phases with lattice parameters close to that of Na_2C_{60} and Na_6C_{60} [10,12]. Given that this transition is reversible, and short range diffusion of sodium ions can result in a significant change in the ^{23}Na spectra, we suggest that at lower temperatures there is migration of some of the sodium ions from less symmetric, larger generalized or octahedral sites into smaller sites of higher tetrahedral symmetry (Scheme 1c). Such migration could potentially result from slight expansion of tetrahedral sites and contraction of octahedral/generalized sites with decreasing temperature.

Variable-temperature ^{23}Na NMR spectra of Na_3C_{60} (A) (Fig. 3A) are significantly different from the ^{23}Na NMR spectra of Na_3C_{60} (B); however, the spectra do

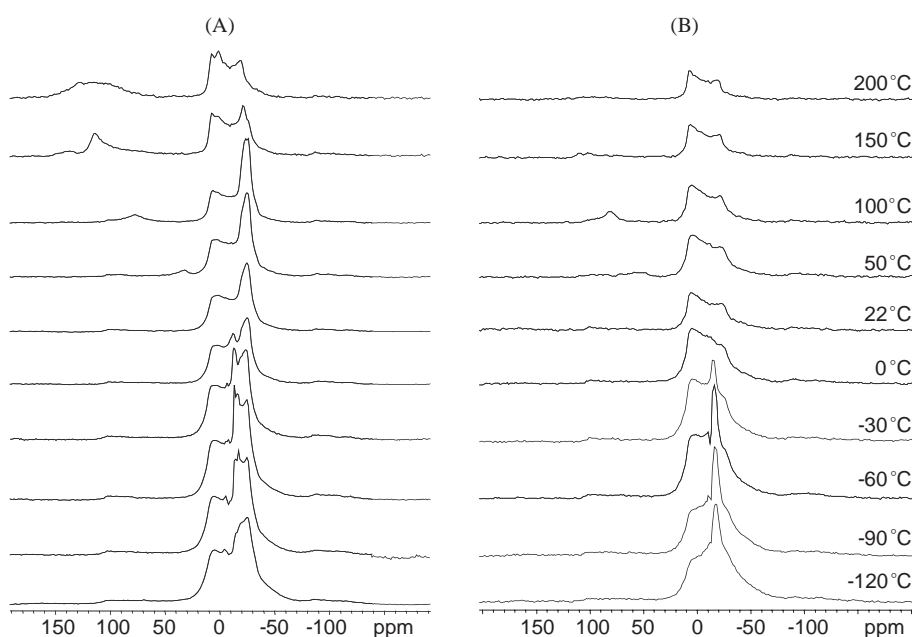


Fig. 3. Variable-temperature ^{23}Na MAS NMR spectra of Na_3C_{60} (A) and Na_3C_{60} (B) at $B_0 = 9.4$ T and $\nu_{\text{rot}} = 12$ kHz.

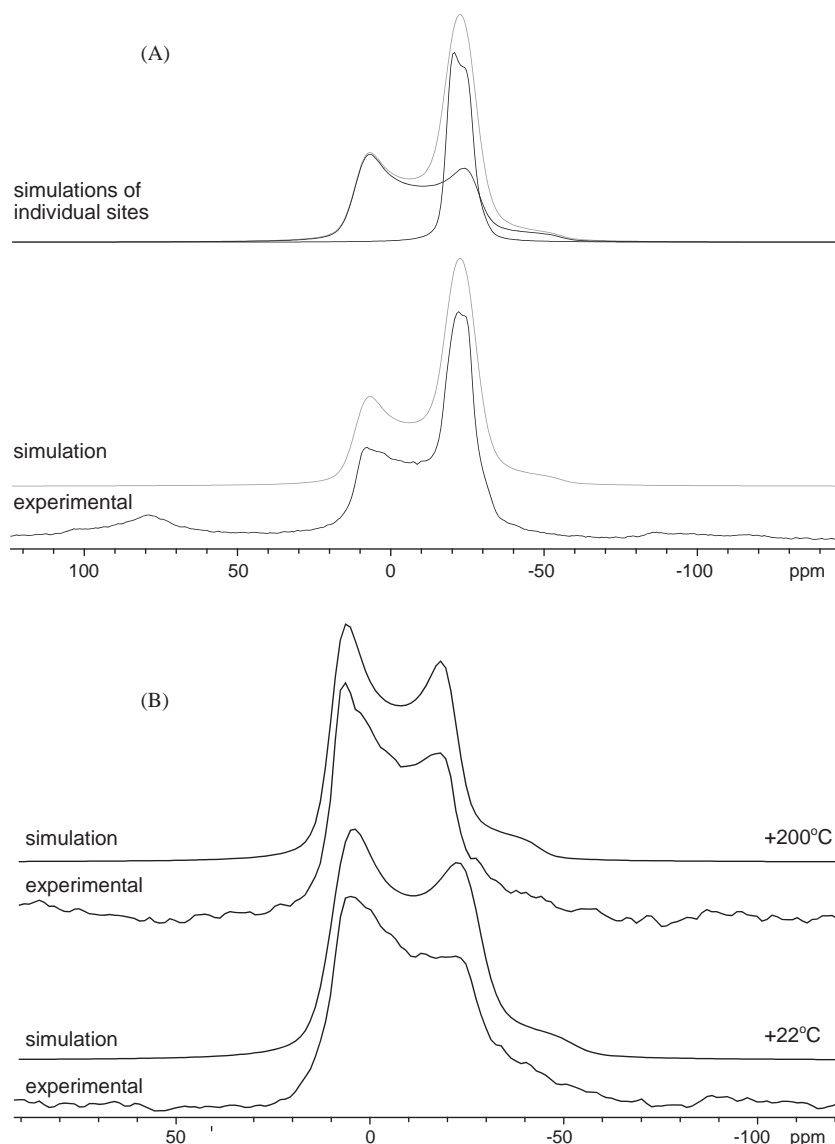


Fig. 4. (A) Experimental and simulated ^{23}Na MAS NMR spectra of Na_3C_{60} (A) at $+100^\circ\text{C}$. (B) *Bottom*: Experimental and simulated ^{23}Na MAS NMR spectra of Na_3C_{60} (B) at $+200^\circ\text{C}$ and $+22^\circ\text{C}$. *Top*: Deconvolution of the simulated powder pattern showing the contributing spectra from individual sites.

share some common features. There is a second-order quadrupolar pattern with a C_Q of ca. 3.4–3.6 MHz and η_Q of ca. 0.1, as well as a sharp resonance at ca. -15 ppm which appears at 0°C and increases in intensity as the temperature is lowered. At 200°C , there is a broad resonance with a center of gravity at ca. $+116$ ppm, which narrows at 150°C , and continues to shift to lower frequency and finally disappears as the temperature is lowered (these are much more intense than those that appear in the ^{23}Na NMR spectra of Na_3C_{60} (B)). There are also some additional low intensity resonances overlapping with the main second-order powder pattern.

Unlike the ^{23}Na spectra of Na_3C_{60} (B), there is a third distinct powder pattern with a narrow second-order lineshape present in spectra of Na_3C_{60} (A) at 100°C and lower and a center of gravity at ca. -23 ppm.

Experimental and simulated ^{23}Na MAS NMR spectra of Na_3C_{60} (A) at 100°C are presented in Fig. 4A. The broad second-order central transition is very similar to that observed for Na_3C_{60} (B), with $C_Q(^{23}\text{Na}) = 3.5(1)$ MHz, $\eta_Q = 0.1(5)$ and $\delta_{\text{iso}}(^{23}\text{Na}) = 21(1)$ ppm. The narrow second-order quadrupolar powder pattern is simulated with $C_Q(^{23}\text{Na}) = 1.6(1)$ MHz, $\eta_Q = 0.1(1)$ and $\delta_{\text{iso}}(^{23}\text{Na}) = -17(1)$ ppm. The integrated areas of the broad and narrow central transition patterns have a ratio of ca. 1.5:1.0. Contrary to the ^{23}Na NMR data for Na_3C_{60} (B) presented above, this data seems to suggest either occupation of octahedral and tetrahedral sites by sodium ions (i.e., the sodium nuclei are in octahedral sites which are relatively asymmetric, and accordingly have large second-order quadrupolar powder patterns,

whereas the sodium nuclei in tetrahedral sites of higher spherical symmetry have reduced quadrupolar interactions and narrower powder patterns), or production of a separate inhomogeneous phase of Na_xC_{60} which has only tetrahedral sodium sites [29]. The relatively high chemical shielding (indicated by the negative chemical shift) at this site may be indicative of close proximity of the sodium nuclei to the fulleride cages (i.e., tetrahedral sites). It has been suggested that alkali ions in the tetrahedral sites of A_3C_{60} materials place a structural constraint on the alkali fulleride, such that hexagonal faces point along [1 1 1] (proper crystallographic notation) directions in the crystal so that the alkali ions are located near the center of aromatic carbon hexagons [13,38]. Similar low-frequency ^{23}Na chemical shifts have been observed for Na nuclei coordinated to substituted and unsubstituted aromatic cyclopentadienyl rings [39].

Summarizing the major points from the ^{23}Na NMR data:

1. ^{23}Na NMR spectra of both (*A*) and (*B*) have a broad second-order quadrupolar powder pattern at all temperatures, indicative of sodium nuclei occupying low-symmetry octahedral sites or so-called “general positions” of low symmetry.
2. Both sets of spectra reveal a sharp resonance that shifts from -15.0 to -17.2 ppm and simultaneously increases in intensity as the temperature is changed from -30°C to -120°C . This is indicative of gradual migration of sodium ions to a site of high spherical electronic symmetry (e.g., tetrahedral sites).
3. The ^{23}Na NMR spectra of Na_3C_{60} (*A*) exhibit the presence of a third resonance with a small second-order quadrupolar powder pattern and low-frequency chemical shift. There are two possible interpretations for this third resonance: (i) occupation of octahedral and tetrahedral interstitial sites at temperatures below 100°C , with increased occupation of tetrahedral sites at lower temperatures, or (ii) production of a local inhomogeneous phase of Na_xC_{60} which would exclusively feature tetrahedral sodium sites.
4. Broad high-frequency resonances are visible in ^{23}Na NMR spectra of both (*A*) and (*B*) at high temperatures, with the peaks being of much higher intensity for the former. It is possible that these resonances correspond to paramagnetic fulleride species, but their precise origin is unknown at this time.
5. All changes in the ^{23}Na NMR spectra with temperature are reversible (heating and cooling to a particular temperature, multiple times, results in the same spectra).

On a final note regarding ^{23}Na NMR, multiple-quantum magic-angle spinning (MQMAS) experiments were also conducted upon these samples, in order to acquire a high-resolution isotropic ^{23}Na NMR spectrum

and aid in resolving the individual sodium sites [40]. Unfortunately, difficulties in obtaining efficient triple-quantum excitation of the broad second-order resonance prevented us from collecting a high quality MQMAS spectrum. Nonetheless, variable-temperature acquisitions (Fig. 3) and spectral simulations (Fig. 4) have enabled us to resolve the individual sites and extract the relevant NMR parameters. Static ^{23}Na NMR spectra were also acquired, but are not presented herein, as individual sites could not consistently be distinguished in these spectra.

3.4. ^{13}C MAS NMR of Na_3C_{60}

Variable-temperature ^{13}C MAS NMR experiments were used to probe the structure and purity of both samples (Fig. 5). The ^{13}C MAS NMR spectra of both *A* and *B* have sharp resonances at ca. 144 ppm, which correspond to C_{60} [15], as well as collections of higher frequency resonances, indicating that these samples are mixtures of segregated C_{60} and “ Na_3C_{60} ” solid phases. Similar spectra have been observed for mixed phases Na_xC_{60} ($x \leq 2$) and C_{60} [18], as well as K_xC_{60} and C_{60} ($x \leq 3$) [15]. At $+200^\circ\text{C}$, the ^{13}C MAS NMR spectrum of Na_3C_{60} (*B*) has a broad resonance at $+180.0(5)$ ppm, which shifts to $+181.2(5)$ ppm at $+150^\circ\text{C}$ (a small resonance at $+177.3(5)$ ppm appears at this point). The corresponding spectra for Na_3C_{60} (*A*) have a series of broad peaks ranging from $+186$ to $+178$ ppm at $+200^\circ\text{C}$, and several discrete resonances at 181.1, 179.7 and 177.3 ppm at $+150^\circ\text{C}$. The spectra acquired at temperatures from 100°C down to -120°C for both samples are similar in appearance, though a greater number of distinct resonances are apparent in the spectra of Na_3C_{60} (*A*). In spectra of both samples, the sharp resonance at $+144.0(4)$ ppm (“free” C_{60}) does not noticeably shift with decreasing temperature. A second sharp resonance starts to grow in intensity at $+100^\circ\text{C}$ and shifts from ca. $+174$ to $+170$ ppm with decreasing temperature. Finally, a third resonance near 180 ppm broadens and apparently splits into two distinct patterns (especially apparent in sample *A*) that shift to high frequency and low frequency (at -120°C they are at $+200$ and $+175$ ppm, respectively). The higher frequency resonances could result from magnetically nonequivalent fulleride carbons or different fulleride species. The former case results from thermally activated symmetry-allowed molecular reorientations of the fullerenes [7], whereas the latter case implies the existence of different fulleride oxidation states, perhaps pointing to non-stoichiometric “ Na_3C_{60} ” (i.e., the mean composition of the sample is Na_3C_{60} , though fulleride species of variable oxidation states, such as Na_xC_{60} , $2.5 < x < 3.5$, may exist, along with the pure C_{60}). Since this behavior is reversible with temperature, it could be that some sort of chemical exchange process is taking place, where the

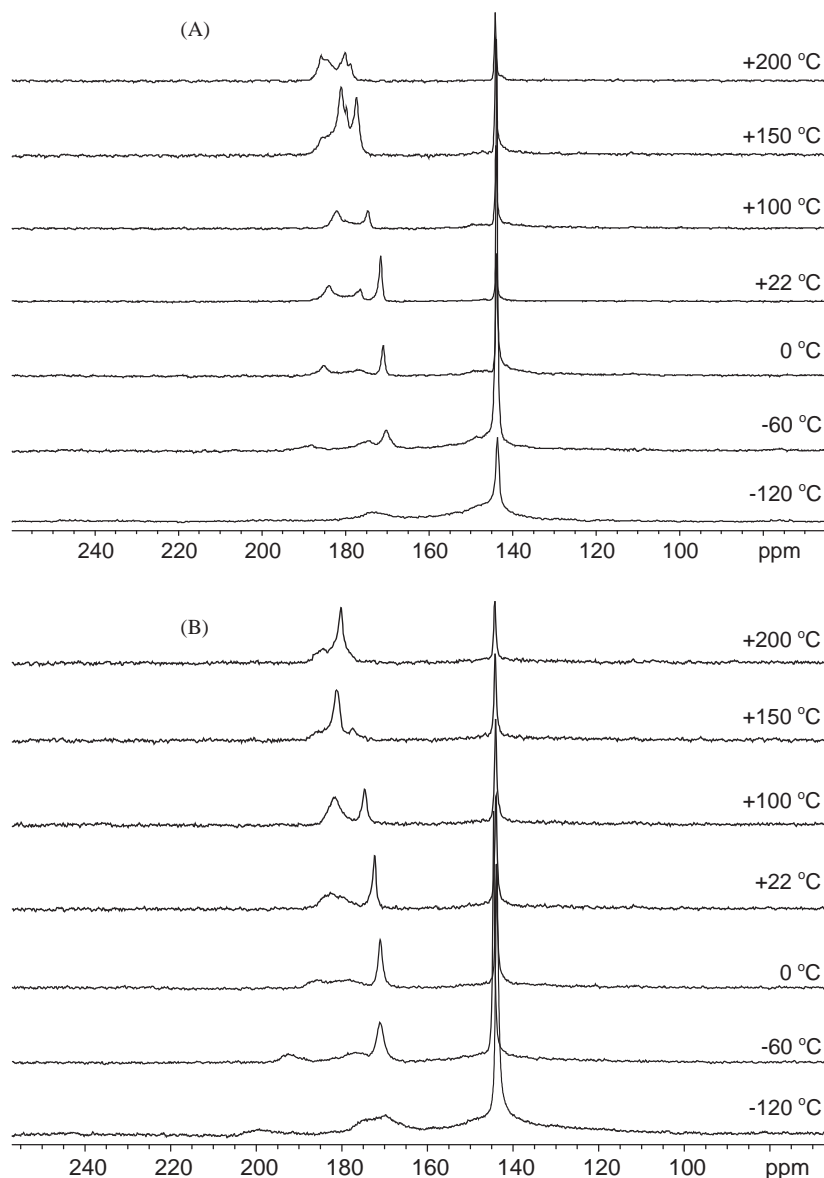


Fig. 5. Variable-temperature ^{13}C MAS NMR spectra of Na_3C_{60} (A) and Na_3C_{60} (B) at $B_0 = 9.4$ T and $\nu_{\text{rot}} = 12$ kHz.

broad high-frequency resonance near 180 ppm (observed for both samples) at $+22^\circ\text{C}$ represents a coalescence point, and distinct chemical shifts can be discerned at lower temperatures.

Since there is not a definitive relationship between the fulleride oxidation state and ^{13}C chemical shift, there is no straightforward assignment of these resonances. For instance, solid-state ^{13}C MAS NMR spectra of Na_2C_{60} and Na_6C_{60} acquired at room temperature exhibit single sharp isotropic resonances at 172 and 176 ppm, respectively [29]. The unusually high frequency shift of the carbon nuclei (the resonances are shifted ca. $+28$ ppm with respect to pure C_{60} , for which $\delta_{\text{iso}} = 143.6$ ppm) is attributed to polarization of the electrons on the carbons. In both cases, small motionally averaged carbon chemical shielding tensors have been measured

as well, indicating the dynamic nature of the fulleride units in these materials. In $\text{Na}_2\text{RbC}_{60}$, two ^{13}C resonances at 189 and 186 ppm are observed at room temperature due to presence of mixed phases (*fcc* and primitive cubic phases, respectively) [32]. At 333 K, only the *fcc* phase is observed (189 ppm resonance), while upon cooling to 253 K, the latter phase is observed (186 ppm). For $\text{Na}_2\text{CsC}_{60}$, ^{13}C shifts range from 185 to 187 ppm [31]. Static ^{13}C NMR spectra have been collected for a variety of alkali metal fullerides, including K_3C_{60} , Rb_xC_{60} ($x = 3, 4, 6$), showing varying motional averaging and apparent isotropic shifts ranging from ca. 165 to 185 ppm. In the case of the spectra presented in Fig. 5, and the other supporting data presented in this paper (i.e., from elemental analysis, Raman spectroscopy and powder XRD), the high

frequency peaks indicate the presence of fulleride species of the form Na_xC_{60} , with $2.5 < x < 3.5$.

Interestingly, the high frequency peaks are broad at low temperatures and sharper at higher temperatures in spectra of both samples. The broadening of the peaks at lower temperatures results from a distribution or “continuum” of chemical shifts due to slower motion of the fulleride and fullerene species [16]. The peaks sharpen at higher temperatures due to motional averaging of the chemical shifts. The broadening does not appear to result from short- or long-range dipolar couplings between ^{13}C and ^{23}Na nuclei, since the widths of the resonances are invariant in spectra acquired at different spinning speeds. Static ^{13}C NMR spectra were relatively unhelpful in obtaining any more information on individual species, since there is a great degree of overlap between spectra from different sites, and an associated loss of S/N due to relatively sizeable carbon chemical shielding anisotropies (for instance, see Refs. [5,7,13] and references therein).

4. Conclusions

Given the differences in NMR spectra acquired for these two samples, it is evident that preparation of phase-pure solid Na_3C_{60} is not trivial and a significant structural difference exists in samples prepared with different annealing times. This is likely due to non-stoichiometry caused by slow diffusion of the sodium ions through the fullerene lattice during synthesis, in which the outer areas of the fullerene crystals are initially over-reduced and the inner areas remain unaffected. In other words, longer annealing times are required to produce an increasingly homogeneous sample. This has been found for mixed alkali fulleride by Kaner and co-workers [9], who reported differences in the kinetic product obtained for $\text{Rb}_2\text{KC}_{60}$ depending on which alkali metal was added first. The results of this study were rationalized on the basis of different diffusion rates of Rb and K through the solid.

The two samples with a mean elemental composition of Na_3C_{60} were synthesized with different annealing times. Raman spectra indicate the presence of the C_{60}^{3-} anion, elemental analysis reveals an elemental composition close to pure Na_3C_{60} and XRD powder patterns indicate almost identical samples. However, solid-state ^{23}Na and ^{13}C NMR experiments reveal significant differences in solid-state structure. ^{23}Na NMR spectra acquired at ambient temperature and higher indicate that the sample prepared with a longer annealing time, Na_3C_{60} (B), seems to have a single general sodium position, whereas the sample prepared with the shorter annealing time, Na_3C_{60} (A), has two distinct sodium sites. Variable-temperature ^{23}Na MAS NMR experiments at temperatures from -120°C to $+200^\circ\text{C}$ on both

samples reveal that some sodium atoms migrate from sites of low spherical symmetry (large octahedral site) to sites of higher symmetry (cramped tetrahedral sites) at lower temperatures. The low-frequency shift of the ^{23}Na NMR resonances are consistent with positioning of sodium ions nestled between aromatic hexagonal faces of the fullerenes. ^{13}C MAS NMR spectra reveal the presence of both fullerene and fulleride species in both samples, with an apparently increased number of different species apparent in the spectra of Na_3C_{60} (A). In ^{13}C MAS NMR spectra of Na_3C_{60} (B) acquired at high temperatures, there are two major resonances: a narrow peak at $+143$ ppm corresponding to C_{60} and a broad peak at $+180$ ppm likely corresponding to Na_3C_{60} and closely related non-stoichiometric species of composition Na_xC_{60} with $2.5 < x < 3.5$. Variable-temperature ^{13}C MAS NMR spectra reveal broad resonances at low temperatures and sharper resonances at higher temperatures, which is indicative of a distribution of chemical shifts at lower temperatures that may result from slowing of fullerene motion. Low temperature ^{13}C MAS NMR experiments reveal separately resolved resonances, suggesting chemical exchange of magnetically distinct fulleride carbons. These results underscore the well-known difficulty in obtaining phase-pure alkali fullerenes and highlight the importance of using solid-state NMR in addition to powder X-ray diffraction, elemental analysis and Raman spectroscopy to fully characterize these materials.

Acknowledgments

We would like to thank the Natural Sciences and Engineering Research Council (NSERC) of Canada for funding this research. RWS would also like to thank the Canadian Foundation for Innovation (CFI), the Ontario Innovation Trust (OIT) and the University of Windsor for funding the Solid-State NMR Laboratory at the University of Windsor. MJW would like to thank the Centre for Catalysis and Materials Research (CCMR) at the University of Windsor for funding in the form of a summer research scholarship. DMA would like to thank the American Chemical Society Petroleum Research Fund (PRF).

References

- [1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, *Nature* 318 (1985) 162.
- [2] D.M. Poirier, T.R. Ohno, G.H. Kroll, Y. Chen, P.J. Benning, J.H. Weaver, L.P.F. Chibante, R.E. Smalley, *Science* 253 (1991) 646.
- [3] C. Gu, F. Stepniak, D.M. Poirier, M.B. Jost, P.J. Benning, Y. Chen, T.R. Ohno, J.L. Martins, J.H. Weaver, J. Fure, R.E. Smalley, *Phys. Rev. B* 45 (1992) 6348.

- [4] R.W. Lof, M.A. Vanveenendaal, B. Koopmans, H.T. Jonkman, G.A. Sawatzky, *Phys. Rev. Lett.* 68 (1992) 3924.
- [5] M.J. Rosseinsky, *Chem. Mater.* 10 (1998) 2665h.
- [6] O. Gunnarsson, E. Koch, R.M. Martin, *Phys. Rev. B* 54 (1996) 11026.
- [7] R. Tycko, *Solid State Nucl. Magn. Reson.* 3 (1994) 303.
- [8] J.B. Wiley, S.M. Huang, S. Cho, F. Diederich, R.L. Whetten, K. Holczer, R.B. Kaner, *Makromolek. Chem.-Macromolec. Symp.* 59 (1992) 389.
- [9] J.B. Wiley, S.M. Huang, S. Cho, K. Holczer, R.L. Whetten, R.B. Kaner, *Synth. Met.* 56 (1993) 3160.
- [10] D.W. Murphy, M.J. Rosseinsky, R.M. Fleming, R. Tycko, A.P. Ramirez, R.C. Haddon, T. Siegrist, G. Dabbagh, J.C. Tully, R.E. Walstedt, *J. Phys. Chem. Solids* 53 (1992) 1321.
- [11] X.H. Chen, J.C. Peng, W.Z. Li, *Physica B* 291 (2000) 285.
- [12] M.J. Rosseinsky, D.W. Murphy, R.M. Fleming, R. Tycko, A.P. Ramirez, T. Siegrist, G. Dabbagh, S.E. Barrett, *Nature* 356 (1992) 416.
- [13] C.H. Pennington, V.A. Stenger, *Rev. Mod. Phys.* 68 (1996) 855.
- [14] T. Yildirim, O. Zhou, J.E. Fischer, N. Bykovetz, R.A. Strongin, M.A. Cichy, A.B. Smith, C.L. Lin, R. Jelinek, *Nature* 360 (1992) 568.
- [15] R. Tycko, R.C. Haddon, G. Dabbagh, S.H. Glarum, D.C. Douglass, A.M. Muzsca, *J. Phys. Chem.* 95 (1991) 518.
- [16] R. Tycko, *J. Phys. Chem. Solids* 54 (1993) 1713.
- [17] J.B. Claridge, A.J. Fowkes, M.J. Rosseinsky, I.D. Watts, *Chem. Mater.* 15 (2003) 1497.
- [18] I.I. Khairullin, W.T. Chang, L.P. Hwang, *Solid State Commun.* 97 (1996) 821.
- [19] R.E. Douthwaite, M.L.H. Green, M.J. Rosseinsky, *Chem. Mater.* 8 (1996) 394.
- [20] D.E. Izotov, V.P. Tarasov, *J. Phys. Chem. B* 106 (2002) 5335.
- [21] M.E. Smith, E.R.H. van Eck, *Prog. Nucl. Magn. Reson. Spectrosc.* 34 (1999) 159.
- [22] A.P.M. Kentgens, *Geoderma* 80 (1997) 271.
- [23] D.L. Bryce, G.M. Bernard, M. Gee, M.D. Lumsden, K. Eichele, R.E. Wasylshen, *Can. J. Anal. Sci. Spectrosc.* 46 (2001) 46.
- [24] M. Tomaselli, B.H. Meier, M. Ricco, T. Shiroka, A. Sartori, *J. Chem. Phys.* 115 (2001) 472.
- [25] S. Sasaki, A. Matsuda, C.W. Chu, *Physica C* 302 (1998) 319.
- [26] C.H. Pennington, C. Hahn, V.A. Stenger, K. Gorny, C.H. Recchia, J.A. Martindale, D.R. Buffinger, R.P. Ziebarth, *Phys. Rev. B* 54 (1996) R6853.
- [27] A.J. Vega, *Encyclopedia of NMR* (1996) 3869.
- [28] D. Freude, in: R.A. Meyers (Ed.), *Encyclopedia of Analytical Chemistry*. Wiley, Chichester, 2000, pp. 12188–12224.
- [29] F. Rachdi, L. Hajji, M. Galtier, T. Yildirim, J.E. Fischer, C. Goze, M. Mehring, *Phys. Rev. B* 56 (1997) 7831.
- [30] Y. Takabayashi, Y. Kubozono, S. Kashino, Y. Iwasa, S. Taga, T. Mitani, H. Ishida, K. Yamada, *Chem. Phys. Lett.* 289 (1998) 193.
- [31] T. Saito, Y. Maniwa, H. Oda, K. Kume, M. Kosaka, I. Hirose, K. Tanigaki, *J. Phys. Soc. Japan* 64 (1995) 4513.
- [32] L. Cristofolini, K. Kordatos, G.A. Lawless, K. Prassides, K. Tanigaki, M.P. Waugh, *Chem. Commun.* (1997) 375.
- [33] M.G. Mitch, S.J. Chase, J.S. Lannin, *Phys. Rev. B* 48 (1993) 8517.
- [34] B.M. Bulychev, V.I. Privalov, A.A. Dityat'ev, *Russ. J. Inorg. Chem.* 45 (2000) 931.
- [35] B. Skadtchenko, M. Trudeau, R.W. Schurko, M.J. Willans, D.M. Antonelli, *Adv. Func. Mater.* 13 (2003) 671.
- [36] R.M. Fleming, A.P. Ramirez, M.J. Rosseinsky, D.W. Murphy, R.C. Haddon, S.M. Zahurak, A.V. Makhija, *Nature* 352 (1991) 787.
- [37] E.A.C. Lucken, *Nuclear Quadrupole Coupling Constants*, Academic Press, New York, 1969.
- [38] P.W. Stephens, L. Mihaly, P.L. Lee, R.L. Whetten, S.M. Huang, R. Kaner, F. Deiderich, K. Holczer, *Nature* 351 (1991) 632.
- [39] M.J. Willans, R.W. Schurko, *J. Phys. Chem. B* 107 (2003) 5144.
- [40] L. Frydman, J.S. Harwood, *J. Am. Chem. Soc.* 117 (1995) 5367.