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NMR evidence for the charge transfer from interstitial NO or O_2 to molecule C_{60} in solid C_{60}

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Abstract. Solid C_{60} was stored in NO and O_2 under high pressure, and the molecule NO and O_2 were found to diffuse into the octahedral interstitial sites in its fcc crystal lattice. Their ^{13}C NMR MAS spectra composed of a primary resonance at 143.7 ppm, accompanied by several minor peaks shifted downfield respectively. The spectra at various temperatures from 210 to 300 K have been measured, and the chemical shifts of the minor peaks referenced to the primary resonance versus inverse temperature show straight lines. But, the lines do not go through origin, and their intercepts are equal to 0.13 ppm or its multiple. Due to a non-zero intercept at high-temperature limit, we proposed that there is a charge transfer from NO and from O_2 to C_{60}. The quantity of the charge transferred has been calculated, that is about 0.065 q_e^- (q_e^- for the elementary charge on an electron).

PACS. 61.48.+c Fullerenes and fullerene-related materials – 76.60.Cq Chemical and Knight shifts – 61.72.Ji Point defects (vacancies, interstitials, color centers, etc.) and defect clusters – 81.40.-z Treatment of materials and its effects on microstructure and properties

1 Introduction

Solid C_{60} can accommodate interstitial atoms or molecules into the tetrahedral and octahedral voids of its face-centered cubic (fcc) lattice. If the dopants were alkaline atoms, it is a fulleride A_xC_{60} (A denoting alkaline ions, $0 < x \leq 6$). The fullerides are insulating, metallic or even superconducting [1,2]. A atoms will reside in the tetrahedral and octahedral voids. For an insulating fulleride ($x = 6$) charge transfer can take place from A atoms to molecules, so that the A atoms become positively charged ions and the C_{60} molecules become negatively charged with predominately localized electrons. ^{13}C nuclear magnetic resonance (NMR) measurements observed the added chemical shift relative to pristine C_{60} (143.7 ppm) [1,3], 43 ppm in K_3C_{60}, 53 ppm in Rb_3C_{60}, 13 ppm in K_6C_{60}, 14 ppm in Rb_6C_{60}. The added shifts result from isotropic Knight-shift contribution at $x = 3$ and chemical shift at $x = 6$. In addition, the alkali ions freeze the ratcheting motion of C_{60} molecules and change the dynamic disorder to "merohedral disorder" [4].

Solid C_{60} has potential application for gas storage. Under high-pressure condition, intercalation of gas molecules has been reported into the octahedral voids of fullerite, but not into the tetrahedral voids due to limited size. These gases had been included, for example, inert gas [5–7], diatomic gas O_2, N_2 [8,9], and polar gas CO [10–12], NO [13] and so on. The guest molecules do not distort the crystal structure, nevertheless they causes a slight expansion of the lattice [10]. In the case of single-atom gas the larger the guest molecule's radius, the longer it stays at the site. Argon can be mostly retained for over a thousand hours, oxygen and nitric oxide for a few hundred hours, neon in under ten hours and helium in a few hours, for C_{60} in the form of compacted pellets under ambient conditions [7]. For solid C_{60} charged with oxygen, ^{13}C magic NMR spectroscopy [8,9] shown a primary resonance at 143.7 ppm and several minor peaks at uniform intervals of 0.7 ppm downfield, and for that with NO the minor peaks at intervals of 0.4 ppm [13]. The appearance of the minor peaks has been explained as paramagnetic interaction of O_2 and NO with ^{13}C on the shell of C_{60} ball [8]. But the high electronegativity of pristine C_{60} implies that charge transfer should take place between the host and guest molecules. Indeed, evidence was found for a weak electrostatic interaction between C_{60} and CO [10,11]. The small amount of charge transfer ($q \sim 0.04q_e^-$, q_e^- is the elementary charge on an electron) from an interstitial oxygen molecule to a C_{60} molecule has also been detected by dielectric method [14]. There exist uncoupled π electrons of O_2 and NO, so we may infer the existence of charge transfer between O_2 (NO) and C_{60}. We will explore this possibility in this paper using NMR method, further.

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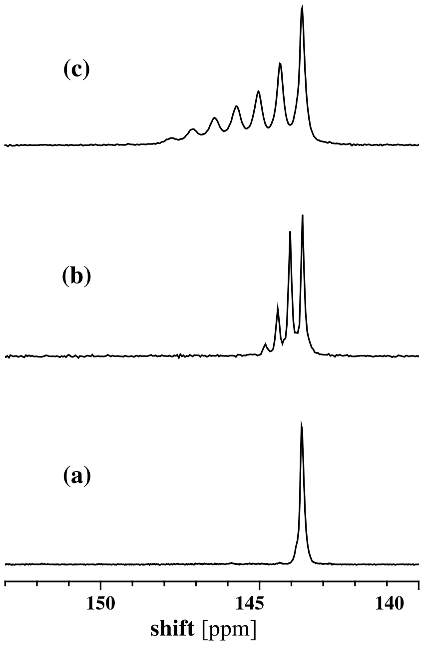

Fig. 1. NMR spectra of pristine C_{60} (a), C_{60} powder charged with NO (b) and oxygen (c).

2 Experimental details

The C_{60} powder of purity better than 99.9%, produced with the contact arc method, which sourced from Wuhan University of China, was annealed at 280 °C in dynamic vacuum for 72 h to have solvent removed. Then, two batches of C_{60} powder was separately placed inside a steel container, to be charged with NO (at 30 bar for 24 hours at 200 °C) and oxygen (0.15 kbar for 7 days at room temperature), respectively. The produced samples are $(NO)_xC_{60}$ and $(O_2)_yC_{60}$, in which x and y represent molar concentration (occupancy of the octahedral sites). These samples were subjected to NMR measurements.

^{13}C NMR measurements proceeded from 210 K to room temperature in a Bruker Avance-300 spectrometer of 7 T (75 MHz) under the condition of magic-angle spinning (MAS) at 3.0 kHz and delay time of 30 s. The probehead of the NMR spectrometer had been calibrated in temperature against the chemical shift of ^{207}Pb in $Pb(NO_3)_2$ according to Bielecki et al. [15]. We allowed approximately 30 minutes for the sample to equilibrate at each temperature.

3 Results

Figure 1 exhibits the ^{13}C MAS NMR spectrum of the pristine C_{60} powder, $(NO)_xC_{60}$ and $(O_2)_yC_{60}$ at room temperature. A primary resonance appeared at 143.7 ppm (Fig. 1a), which relates to freely rotating C_{60}. Charging with NO resulted in two secondary resonances at 144.1 and 144.5 ppm downfield respectively, as shown in Figure 1b. The spin-lattice relaxation time T_1 of the primary peak was 65.11 ± 0.01 s, whereas that for the nearest minor peak was 11.25 ± 0.03 s, at field strength of 7 T. Figure 1c exhibits the spectrum of the powder charged with oxygen. Five secondary resonances appeared at uniform intervals of 0.7 ppm. The number of the resonances is corresponding to the filling of 0 to 2 or 5 of the adjacent octahedral with NO or O_2 [8,13]. If we denote the height of each resonance by I_n, $n = 0$ to 6, where I_0 corresponds to that of the primary resonance, etc., then following the analysis of the O_2 case by Assink et al. [8], we can evaluate the fraction of C_{60} molecules surrounded by n O_2 or NO molecules as $F_n = I_n / \sum I_n$. The proportion of O_2 or NO occupied sites is then simply $F^* = \sum nF_n/6$, where the division by 6 is to eliminate multiply counting since each O_2 or NO molecule is associated with six adjacent C_{60}. The results are $x = 0.10$ and $y = 0.20$, corresponding to the cases of Figures 1b and 1c, separately.

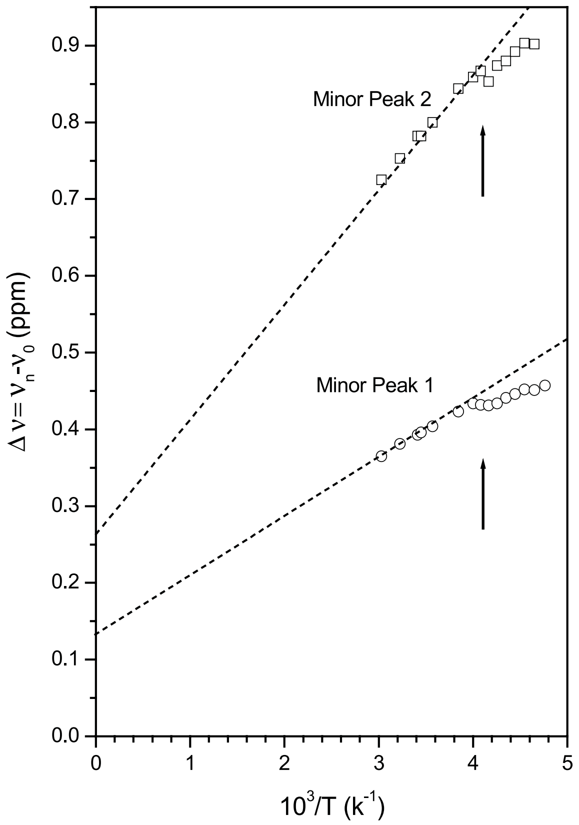

Fig. 2. The chemical shift of the various secondary resonances ν_n of C_{60} powder charged with NO referenced to that of the primary resonance ν_0, as a function of inverse temperature.

Figures 2 and 3 depict the chemical shift of the various secondary resonances in the Figures 1b and 1c referenced to that of the primary resonance, as a function of inverse temperature. The least-squares fit of the data yields a straight line for each resonance, which can be expressed by an equation

$$\Delta_n = A_n/T + 0.13n, \; n = 1 \text{ to } 6. \qquad (1)$$

Their offsets are 0.13, 0.26, 0.39 ppm, and so on. The offset increases linearly with the number of the adjacent interstitial molecules. Because the sample's temperature

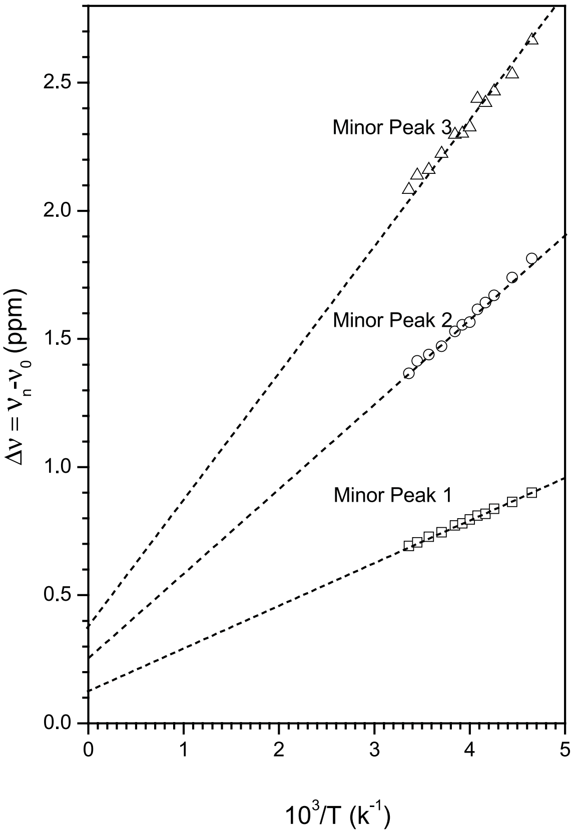

Fig. 3. The chemical shift of the various secondary resonances ν_n of C_{60} powder charged with O_2 referenced to that of the primary resonance ν_0, as a function of inverse temperature.

has been calibrated, the error of the temperature on the residual offsets can be excluded. Subtracted the offsets from the correspondent line, Δ_n will be obey the Curie's law.

In Figure 2, upon heating a slight drop appeared at 240 K obviously, which is attributed to the order-disorder phase transition [16]. NO was found to depress the transition temperature T_c from normal value of 260 K, which agreement with our previous result of dielectric measurement [13]. But this slight drop correlated with the transition has not been observed in Figure 3 for a sample charged with O_2.

4 Discussion

In the case of C_{60} charged with O_2, Assink et al. [8] had explained the position of the minor resonances in terms of paramagnetic shift as the weak paramagnetism of molecular oxygen. But Belahmer et al. [17] proposed that there still exists the possibility of having even a small charge transfer between O_2 and the C_{60} molecules, with a corresponding shift of the resonance. They further expected such a shift to be very small, because of supposed much less than one electron.

A_xC_{60} (A denoting alkaline ions, $x = 1$ to 6) is superconducting or insulating dependent on the mole ratio x. For $x = 6$ the insulating behavior is expected due to full filling of the t_{1u} band. Since K_6C_{60} and Rb_6C_{60} is an insulator like undoped C_{60}, their ^{13}C shift of NMR must be entirely a chemical shift [18]. We list here the following data obtained at room temperature: C_{60} (143 ppm), K_6C_{60} (156 ppm), Rb_6C_{60} (157 ppm) [3]. According to analysis by Zimmer et al. [3], six electrons in the $x = 6$ has transferred case to the C_{60} molecule, which results in a total chemical shift of 12 ppm relative to the undoped C_{60}. Averagely, one electron contributes 2 ppm to the chemical shift i.e. 2 ppm/electron.

Molecular oxygen is paramagnetic due to it contains two π electrons with parallel spin. Nitric oxide (NO) is also paramagnetic with an unpaired π electron-spin, the square of its magnetic moment being half of that for oxygen [19]. O_2 and NO charging separately produce a maximum of six secondary peaks downfield of the primary (the figures omitted here), because each C_{60} molecule is associated with six octahedral voids. The molecular oxygen would tumble within the octahedral voids [8]. Meanwhile, the paramagnetic molecules execute a spin-hyperfine interaction to ^{13}C nucleus of C_{60} shell. The unpaired electron-spin of the paramagnetic molecules will induce a spin polarization of the ^{13}C atomic $2s$ orbitals. The ^{13}C nuclear spin interacts with the unpaired electron-spin density in $2s$ orbitals at the position of the ^{13}C nucleus, which is the Fermi contact interaction [18]. As we known, the paramagnetic shift produced by the Fermi contact interaction, should obey Curie's law. We have measured the shift of the minor peaks as a function of inverse temperature, and found the temperature-dependent shift is a straight line as shown in Figures 2 and 3. The line can be described in the form of equation (1). The second term of the equation is a constant $0.13n$, which represents a departure from the Curie's law. So, the shift is composed of two terms, one the Curie's contribution and the other a constant which then depends on the number of nearest O_2 and NO molecules around each C_{60}.

The second term of equation (1) is independent of temperature. In Analog to the case of A_xC_{60}, we propose it origins from charge transfer. Because of electronegative difference of guest (O_2 and NO) from host (C_{60}) molecule, the O_2 and NO molecule in the octahedral site of C_{60} lattice could denote their electrons to the C_{60} molecule. From the value 0.13 ppm of the second term of equation (1) at $n = 1$ and ratio 2 ppm/electron, we arrive at $q = 0.065q_e^-$, where q stands for transferred charge and q_e^- for the elementary charge on an electron. The proportion of guest molecular occupied sites is $F^* = \sum nF_n/6$. When $n = 6$ and $F_n = 1$, the proportion is $F^* = 1$. In this case, all of octahedral sites of C_{60} lattice would have been filled and the molar ratio of O_2(or NO):C_{60} would be 1:1, and the largest transferred charge value should be $6 \times 0.065q_e^- = 0.39q_e^-$. This ratio had not been achieved from experiment even C_{60} sample charged with guest gas under a high pressure of ~kbar [8]. Under ambient condition, oxygen readily diffuses into the octahedral sites of C_{60} fcc lattice but its amount is very small (about 1%). In this concentration, ^{13}C MAS NMR spectrum shows only one secondary resonance at downfield of the primary resonance, which implies the C_{60} molecule surrounded by one guest molecule. To expose a C_{60} film for air resulted in the small amount of interstitial O_2, then, dielectric experiment [14] had detected the small value of transferred charge $q = 0.04q_e^-$ from O_2 to C_{60} molecule. This value is very close to our data $q = 0.065q_e^-$ at $n = 1$.

We note that although the chemical shifts versus the inverse temperature, such as presented in Figure 2, shows the linear dependence, and the slight drop appears close to 240 K. This drop should be attributed to the order-disorder phase transition [13,16], because NO was found to depress the transition temperature T_c from normal value of 260 K. However, this sign of the transition has not been seen in solid C_{60} charged with O_2, as shown in Figure 3. In our previous works [9,13], different effect of nitride oxide from oxygen on impedance spectra at the transition had been observed by dielectric method. The nitride oxide was found to reduce the drop in dielectric constant $\varepsilon\prime$ at the transition, and oxygen to enlarge it, which means that oxygen enhances order-parameters fluctuation below T_c but nitride oxide depress it. These phenomena would be explained as that NO bind tighter than O_2 with C_{60}, due to the former is dipolar molecule with a permanent dipole moment. The study about details is in progress.

5 Conclusion

We proposed that there is a charge transfer from NO and from O_2 to C_{60}. The quantity of the charge transferred has been calculated, that is about $0.065q_e^-$ (q_e^- for the elementary charge on an electron).

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