Nanosegregation in Na_2C_{60}

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Abstract.
There is continuous interest in the nature of alkali metal fullerides containing C_{60}^{4-} and C_{60}^{2-}, because these compounds are believed to be nonmagnetic Mott–Jahn–Teller insulators. This idea could be verified in the case of A_4C_{60}, but Na_2C_{60} is more controversial. By comparing the results of infrared spectroscopy and X-ray diffraction, we found that Na_2C_{60} is segregated into 3-10 nm large regions. The two main phases of the material are insulating C_{60} and metallic Na_3C_{60}. We found by neutron scattering that the diffusion of sodium ions becomes faster on heating. Above 470 K Na_2C_{60} is homogeneous and we show IR spectroscopic evidence of a Jahn–Teller distorted C_{60}^{2-} anion.

INTRODUCTION

The proposed [1] Mott–Jahn–Teller ground state of A_4C_{60} (A = K, Rb, Cs) fullerides was experimentally verified by EELS [2], NMR [3] and infrared (IR) [4] spectroscopies. Theory predicts a similar effect in fullerides with C_{60}^{2-} ions, the electron-hole inverted analogue of C_{60}^{4-}. Na_2C_{60} is the only known alkali-metal fulleride that is believed to contain the C_{60}^{2-} dianion and there were several attempts to verify the Mott–Jahn–Teller insulating ground state in this compound as well. Experimental results were not unambiguous [3], e.g. a very weak metallic behavior was found in Na_2C_{60}, but it was concluded that K_4C_{60} and Na_2C_{60} have essentially the same Mott–Jahn–Teller ground state.

In contrast, our infrared, X-ray and neutron scattering experiments indicate that Na_2C_{60} is not a good model system to investigate the ground state of A_2C_{60} fullerides. Above 470 K Na_2C_{60} is homogeneous and at high temperatures we find indication for Jahn–Teller distorted C_{60}^{2-} ions. The IR spectroscopy and X-ray diffraction results at ambient temperatures show, however, a nanosegregation of Na_2C_{60} into two phases.

EXPERIMENTAL

Na_2C_{60} was obtained by the reaction of stoichiometric amounts of Na and C_{60} at high temperature in a stainless steel capsule. The typical annealing sequence was first 23 days
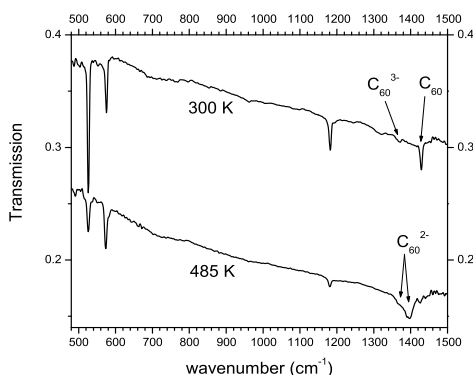
FIGURE 1. The IR spectra of Na_2C_{60} at 300 K and at 485 K. At high temperature the absorption of the $T_{1u}(4)$ mode could be fitted with two Lorentzians centered at the indicated positions, corresponding to C_{60}^{2-}, while at 300 K lines corresponding to C_{60} and C_{60}^{3-} appear.

at 350 °C and then 7 days at 450 °C. To homogenize the samples, we reground them about once every five days. Due to the air sensitivity of Na_2C_{60}, the reaction and the handling of the samples were carried out under inert atmosphere.

The sample was characterized by X-ray diffraction, which showed the material to be single phase $Pa\bar{3}$ (simple cubic) Na_2C_{60}. This result is identical to those in the literature [5].

Infrared measurements were performed on pressed KBr pellets in a Bruker IFS 28 FTIR instrument in a cryostat under dynamic vacuum. For neutron scattering measurements 1.2 g of Na_2C_{60} powder was placed in an annular aluminum sample holder. Temperature dependent elastic fixed-window scans were taken on the High Flux Backscattering Spectrometer of the NIST Center for Neutron Scattering [6]. In this measurement, the incident neutron energy was fixed at 2.08 meV and scattering processes were detected near the elastic line within the 1 μeV energy window of the resolution of the instrument[7]. Thus when a dynamic process became faster than the corresponding timescale of 0.8 ns, the measured intensity decreased.

RESULTS AND DISCUSSION

The charge state of C_{60} anions can be evaluated from the quasilinear relationship between the charge state and the line position of the $T_{1u}(4)$ IR mode [8]. We expect from this relation a line of C_{60}^{2-} at about 1380 cm^{-1}. Contrary to this expectation, there is no such line in the measured 300 K spectrum (Fig. 1) instead lines characteristic of neutral C_{60} and of C_{60}^{3-} appear. In contrast to the narrow line of C_{60}, that of C_{60}^{3-} is smeared into a broad line. This kind of line broadening is common for A_3C_{60} phases and is caused by metallic electrons. The metallic character of an aggregate as small as a few C_{60}^{3-} mole-

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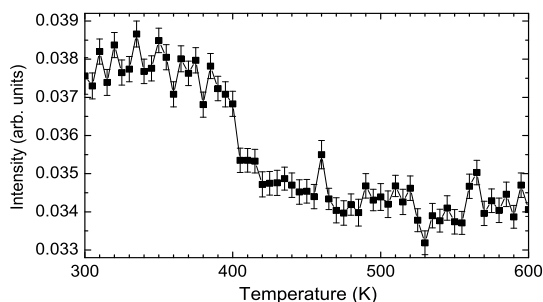
FIGURE 2. Elastic fixed window scan intensity of Na_2C_{60} at $Q = 1\mathring{A}^{-1}$.

cules is sufficient to broaden the IR line. Thus C_{60}^{3-} and C_{60} are not homogeneously distributed in the crystal lattice.

The observation of segregated Na_3C_{60} and C_{60} regions in the material by IR spectroscopy apparently contradicts the observation of a single phase by X-ray diffraction. However, if the size of segregated regions is smaller than about 10 nm, then X-ray diffraction cannot resolve the two phases but detects their average. Thus from the comparison of IR and X-ray diffraction measurements we conclude that Na_2C_{60} is nanosegregated at ambient temperatures.

The amount of neutral C_{60} in the material could be determined by its selective extraction with toluene. The concentration of the obtained C_{60} solution was measured with high-pressure liquid chromatography (HPLC). From this we could estimate the C_{60} content to be 26-33 % C_{60} in the nominally Na_2C_{60} material.

Heating the material to high temperatures proves that the stoichiometry of the sample is indeed Na_2C_{60} and that at high temperatures there is no neutral C_{60} left. The lines of neutral C_{60} disappear above 470 K, and a pair of lines appears at 1369 cm^{-1} and 1394 cm^{-1} (Fig. 1). This line pair is at about the expected frequency for the $T_{1u}(4)$ line of C_{60}^{2-}. Thus at room temperature the C_{60} content is not material left unreacted during the high temperature synthesis, but rather the product of the reaction $3C_{60}^{2-} \longrightarrow C_{60} + 2C_{60}^{3-}$ taking place on cooling after preparation. This reaction is reversible on heating and cooling, though a total retransformation at ambient temperature following treatment at high temperature is reached only after about two weeks.

The line pair of C_{60}^{2-} is the lower frequency analogue of the line pair of C_{60}^{4-} [4], indicating that C_{60}^{2-} is distorted to a D_{3d} or a D_{5d} geometry due to the molecular Jahn–Teller effect [4].

The synproportion reaction on heating ought to be accompanied by diffusion of Na ions in the lattice. This could be proven by neutron scattering. Figure 2 shows the temperature dependence of the elastic line at $Q = 1\mathring{A}^{-1}$. The intensity shows a Debye-Waller-type overall decrease, but has an unusual drop near 400 K. We interpret this with the increase of the jump diffusion of sodium ions between tetrahedral and off-centered octahedral sites. Above 400 K it becomes fast enough to be resolved by the

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instrument and the incoherent scattering contribution of the sodium ions is removed from the fixed-window intensity. The different transition temperatures found in the IR and neutron measurements may be due to the different timescales.

CONCLUSION

We propose that Na_2C_{60} is nanosegregated at room temperature. The two main phases of Na_2C_{60} are insulating C_{60} and metallic Na_3C_{60}. The size of the homogeneous regions is about 3-10 nm. The segregation disappears on heating when the jump diffusion of sodium ions becomes faster. A similar segregated phase, the "intermediate phase" is known for KC_{60} [9]. In Na_2C_{60} at high temperatures, the sodium distribution is homogeneous and a Jahn–Teller distortion of C_{60}^{2-} ions is observed.

ACKNOWLEDGMENTS

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