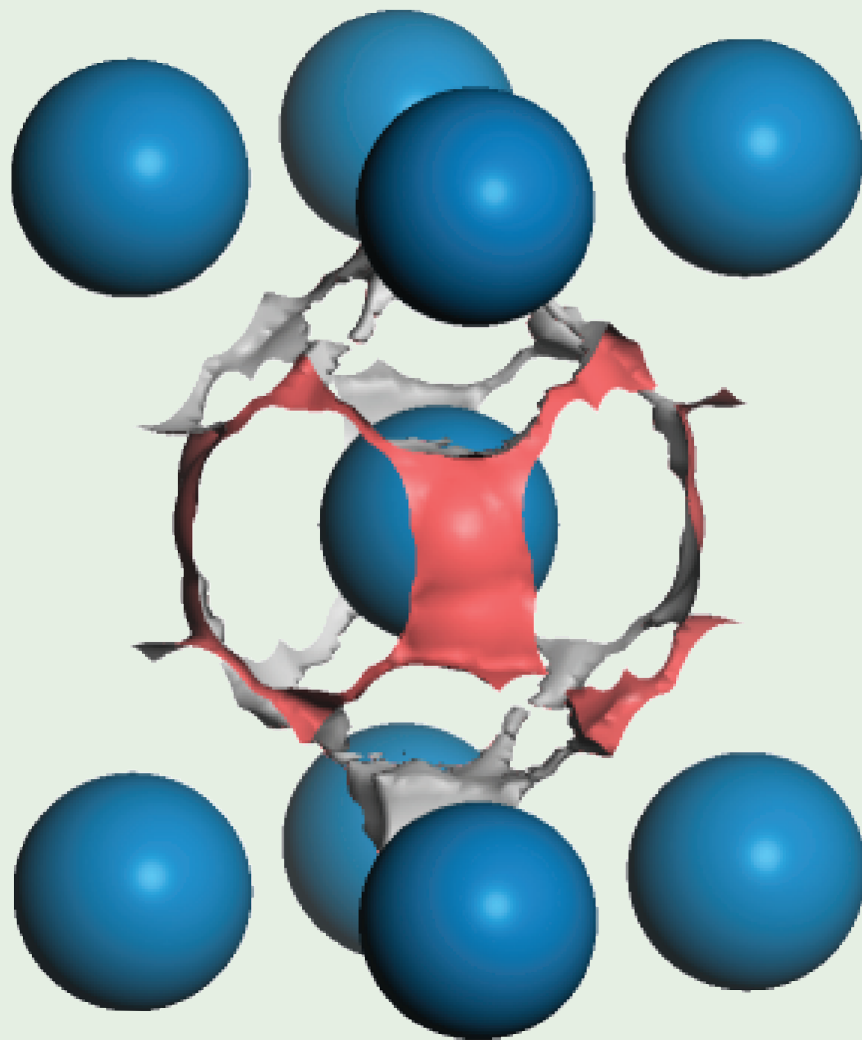


PHYSICAL REVIEW LETTERS

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Articles published week ending 10 APRIL 2009



Published by the
American Physical Society

APS
physics

Volume 102, Number 14

Superionic Conductivity in the Li_4C_{60} Fulleride Polymer

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(Received 12 January 2009; published 8 April 2009)

We report on the extraordinary superionic conductivity in the fulleride polymer Li_4C_{60} , a crystalline material with no disorder. ^7Li , NMR, and dc frequency dependent conductivity show uncorrelated ionic hopping across small energy barriers ($\Delta E_a \sim 200$ meV) and an ionic conductivity of 10^{-2} S/cm at room temperature, higher than in “standard” ionic conductors. *Ab initio* calculations of the molecular structure find intrinsic unoccupied interstitial sites that can be filled by Li^+ cations in stoichiometric Li_4C_{60} even at low temperatures. The low energy required for the occupation of these sites allows a sizable Li^+ diffusion above 130 K. The results suggest novel application of lithium intercalated fullerides as electrodes in Li ions batteries.

DOI: [10.1103/PhysRevLett.102.145901](https://doi.org/10.1103/PhysRevLett.102.145901)

PACS numbers: 66.30.H-, 72.20.-i, 81.05.Tp, 82.35.Lr

High ionic conductivity in solid-state phases is usually observed in strongly disordered or glassy compounds with a large concentration of ions and unoccupied sites in which the ions can diffuse [1]. In these materials the unoccupied interstitial sites are not intrinsic to the crystalline structure, but are due to defects or imperfect stoichiometry. The ionic conductivity of these “superionic” compounds is comparable to what is observed in the molten state. In this Letter we report an exceptionally high ionic conductivity in the Li_4C_{60} fulleride which has an ordered crystalline structure.

The fcc crystal lattice of pure C_{60} has two tetrahedral and one, approximately twice as large, octahedral interstitial voids per molecular unit, which easily accommodate even the largest alkali atoms. However, the limited size of the trigonal aperture connecting the interstitial sites prevents the diffusion of alkali atoms larger than Na without a reorganization of the fullerene molecular positions by, e.g., motion of dislocations. For this reason, ionic conductivity was not observed in fullerides in spite of the large amount of free space in their crystalline structure. Diffusion of Na^+ ions was reported in nominal Na_2C_{60} fulleride only at the relatively high temperature of 400 K [2].

In this Letter we show that this picture changes dramatically for the low temperature phase ($T < 400$ K) of Li_4C_{60} fulleride, which has a two-dimensional polymer structure. The polymer layer is a rectangular lattice of C_{60} molecules interconnected by pairs of [2 + 2] cycloaddition C-C bonds and single C-C bonds along two perpendicular directions [3]. The interfullerene covalent bonds distort

the pristine fcc lattice into monoclinic (space group $I2/m$). Two Li^+ ions of the formula unit occupy the tetrahedral (1/2, 0, 3/4) sites of the cubic parent structure, while the other two Li^+ ions doubly occupy the corresponding octahedral sites (0, 0, 1/2) [4].

Li_4C_{60} is a band insulator at low temperature, as opposed to the other alkali intercalated fulleride polymers, which are metallic throughout a wide temperature range. The high temperature monomer phase, stable above 590 K, is a fcc metal; in this case the fcc arrangement of the lattice leads to an unfilled electronic band and a metallic character [5,6]. Incidentally, this represents the only A_4C_{60} (A = alkali metal) monomer fulleride to be metallic under normal conditions.

We show that in polymeric Li_4C_{60} the Li^+ ions easily overcome the low intersite barriers. The activation energy for Li ion diffusion, $\Delta E_a = 200$ meV, measured by both conductivity and magnetic resonance, is considerably lower than activation energies of most superionic conductors. Furthermore, the large octahedral site can host several ions. Our *ab initio* calculation predicts two unoccupied Li^+ interstitial sites in addition to the two already occupied sites in voids derived from the octahedral sites. The configurations in which more than two cations occupy the octahedral site have low energies and allow Li^+ diffusion in the lattice even at low temperatures ($T > 130$ K). These particularities of the structure lead to an exceptionally high ionic conductivity, $\sigma \sim 10^{-2}$ S/cm, at room temperature. This value is 1 order of magnitude larger

than conductivities of the well known NASICON-type ionic conductors [7], suggesting the possible application of polymeric Li_4C_{60} as a Li ion battery component.

Polymeric Li_4C_{60} samples were prepared by thermal decomposition of Li azide as previously reported [3]. The dc and frequency dependent conductivities were measured on pressed pellets electrically contacted by silver paint in an Ar glove box. The air sensitivity of alkali fullerenes required us to operate under strict oxygen and moisture free conditions with less than 1 ppm O_2 and H_2O . No reaction of the paint with the pellet surface was detected. The sign of the dc current was inverted every 200 msec to prevent Li^+ ion accumulation at the electrodes. ^7Li NMR was measured on powder samples using an Apollo Tecmag spectrometer equipped with a Bruker probe head optimized for solid-state experiments. The compound was sealed in a quartz tube under He atmosphere. The nuclear relaxation rate was measured with the saturation recovery technique. The CASTEP plane wave density functional theory (DFT) code [8] was used for the *Ab initio* calculations of the molecular structure.

The temperature dependence of the dc conductivity between 80 and 330 K is shown in Fig. 1. Below 130 K, the conductivity is nearly temperature independent and has a low value of about 10^{-7} S/cm. Above 130 K the conductivity increases with temperature up to 10^{-2} S/cm at room temperature and follows an Arrhenius law. We find an activation energy of $E_a^{\text{dc}} = 240$ meV, surprisingly low for an ionic conductor, showing that the energy barriers for Li^+ ion diffusion are low in this system. We suggest that the conductivity above 130 K is dominated by ionic conductivity. As detailed below, this ionic character of the dc conductivity is confirmed by finite frequency (ac) conductivity and ^7Li NMR spin-lattice relaxation measurements and is predicted by the structural calculations. Below

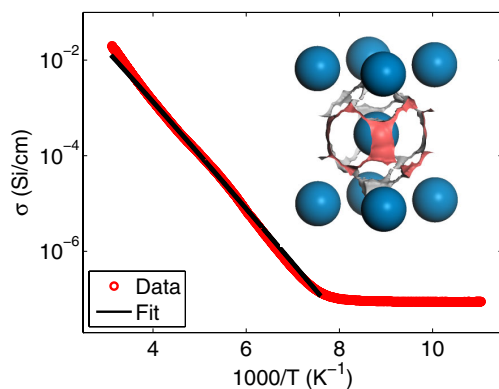


FIG. 1 (color online). Temperature dependence of dc conductivity of polymeric Li_4C_{60} . The low temperature plateau corresponds to a sample resistance of 20 M Ω . Inset: Illustration of the possible paths for Li^+ ion diffusion in polymeric Li_4C_{60} . Blue balls are fullerene molecules, the pink/grey (medium grey/light grey) region is the volume which the centers of diffusing Li ions can occupy (see text).

130 K, Li^+ ions are frozen in their crystallographic positions [4] and the residual conductivity is not an intrinsic electronic conductivity as the band gap is large, our electronic structure calculation gives a value of 0.77 eV. Thus the residual metallic conductivity arises probably from defects in the structure.

Impedance was measured in the 10^3 – 10^6 Hz frequency range at three different temperatures, 190 K, 220 K, and 246 K. The frequency dependence of the imaginary part of the impedance is presented in the upper panel of Fig. 2. The appearance of a single loss peak for all investigated temperatures shows that there is a single dipolar relaxation mechanism, which we attribute to bulk Li^+ ion conduction through sites separated by rather well defined barriers. As opposed to disordered ionic conductors, the loss peaks are quite well described by an ideal Debye process where the imaginary part of the impedance Z'' depends on a single relaxation time, τ , and follows $Z'' \sim \omega\tau/(1 + \omega^2\tau^2)$. The 1.14 decades width at half-height of the peak is also in perfect agreement with the Debye model. The Arrhenius plot of the relaxation time τ , obtained from the inverse of the peak frequency as a function of temperature, is shown in the lower right panel. The observed linear behavior confirms the Debye-like relaxation mechanism of the dipoles responsible for the peak in Z'' . The fitted activation energy $E_a^{\text{ac}} = 209$ meV is in good agreement with the value extracted from dc conductivity measurements. The complex impedance (Cole-Cole) plots (lower left panel of Fig. 2) at the three temperatures investigated are single-peaked broad arcs terminating at the origin, which indicates the absence of resistance and/or capacitance in series in the equivalent circuit representation of the sample. This excludes possible contributions from ill defined dispersive

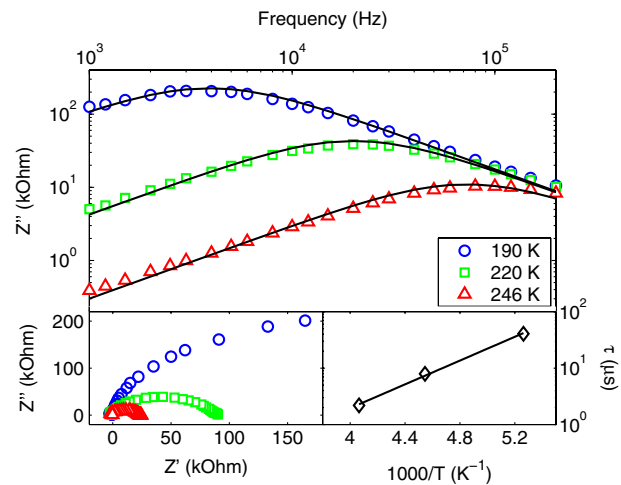


FIG. 2 (color online). Upper panel: frequency dependence of the imaginary part of the impedance, Z'' , at different temperatures. The solid line represents the fit with an ideal Debye loss function. Lower panel, left: corresponding Cole-Cole diagrams. Lower panel, right: correlation times extracted from the frequency dependence of Z'' .

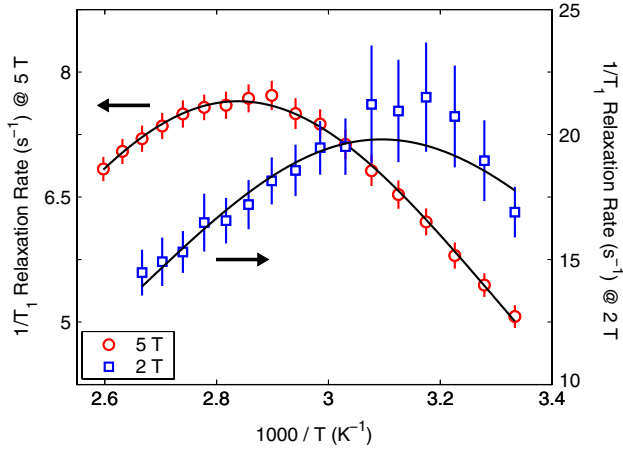


FIG. 3 (color online). Temperature dependence of ${}^7\text{Li}$ NMR relaxation rate in Li_4C_{60} at the field of 2 T (right scale, $\omega_0/2\pi = 33.10$ MHz) and 5 T (left scale, $\omega_0/2\pi = 82.75$ MHz).

regions, which could arise from the accumulation of the ions at the electrodes or at the grain boundaries.

Li^+ ion diffusion also contributes to the relaxation of the Li nuclear magnetization due to the interaction between the nuclear quadrupole moment and the fluctuating local electric field gradients. We measured the ${}^7\text{Li}$ NMR spin-lattice relaxation time in polymeric Li_4C_{60} above room temperature, between 300 K and 380 K. In this temperature range the quadrupolar ($I({}^7\text{Li}) = 3/2$) powder pattern is motionally narrowed into a single line [6]. As expected from theory, a single-exponential spin-lattice relaxation is observed [9].

In Fig. 3 we show the temperature dependence of the ${}^7\text{Li}$ spin-lattice relaxation rate $R = 1/T_1$, measured at two different applied magnetic fields ($H = 2$ and 5 T). A peak appears in the spin-lattice relaxation rates at 325 K and 352 K for fields of 2 T and 5 T ($\omega_0/2\pi = 33.10$ MHz and 82.75 MHz Larmor frequencies), respectively. In the framework of the Bloembergen-Purcell-Pound (BPP) theory the diffusion correlation time $\tau(T)$ at these temperatures can be roughly estimated as the inverse of Larmor angular frequencies $\omega_0\tau = 1$. The obtained values are $\tau(323 \text{ K}) = 4.8$ ns and $\tau(352 \text{ K}) = 1.9$ ns.

Actually in the BPP model the relaxation rate is expressed in terms of τ as [10]: $R = k[\frac{\tau}{1+\omega_0^2\tau^2} + \frac{4\tau}{1+4\omega_0^2\tau^2}]$. Following the results of the ac measurements, we assumed the temperature dependence of the correlation time to be activated-like, $\tau = \tau_0^{\text{NMR}} e^{E_a/k_B T}$. The solid lines in Fig. 3 represent the fit of this model to the measured values with the parameters displayed in Table I. The measurements at 2 T are more affected by electronic noise and the data have a larger scatter than the 5 T data. The high quality of the fit at 5 T clearly confirms the model. The relaxation rate peak is symmetric, in contradistinction with disordered ionic conductors in which the peak is asymmetric as a result of either a distribution of the activation energies [11] or the onset of correlated ionic diffusion [12]. This is consistent

TABLE I. Fitted parameters for the correlation times describing Li motion in Li_4C_{60} probed with different techniques.

Technique	Temper./Magn.Field	τ_0 (ps)	E_a (meV)
NMR	300–380 K, 2 T	3.0	191
NMR	300–380 K, 5 T	2.4	189
dc conductivity	80–330 K	-	240
ac conductivity	190 K, 220 K, 246 K	119	209

with the crystalline nature of Li_4C_{60} and the relatively low concentration of Li^+ ions.

The calculated DFT optimized structure of Li_4C_{60} confirmed the X-ray diffraction results reported previously [4], with the important exception of the position of the cations in the octahedral site. As shown in Fig. 4, the calculated positions are slightly shifted along the a axis direction with respect to positions determined experimentally. In the diffraction experiments, a precise localization of the small Li ions is made difficult by their small scattering length and high thermal factors. We believe that the displacement along the a axis found in the calculation was too small to be detected by x-ray diffraction.

Interestingly, the calculated structure allows for two new possible Li^+ interstitial positions within the octahedral site, at the corners of an imaginary rectangle in the ac plane. We computed the energy with respect to the optimized structure of configurations with various octahedral Li occupancies (see Table II), using a 128 atoms unit cell. For each configuration the number of Li atoms in the different sites was varied but the total number of Li atoms was always 8, in order to guarantee the correct stoichiometry. All geometries of the possible configurations were relaxed until the force on each atom was less than

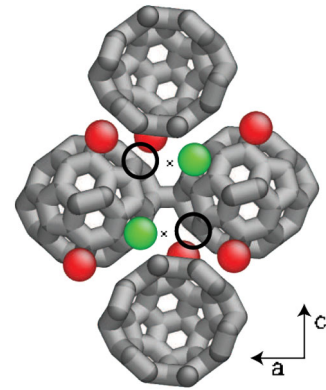


FIG. 4 (color online). Occupied [green (light grey) balls] and unoccupied (empty circles) Li^+ interstitial positions in the octahedral site according to *ab initio* calculations. These four sites lie on the $b = 0$ plane at coordinates $(0.18, 0, 0.36)_{\text{occup}}$ and $(0.13, 0, 0.64)_{\text{unoccup}}$ respectively. Li^+ ions in the tetrahedral sites are indicated by red (dark grey) balls. The positions of the Li^+ ions reported in a previous x-ray diffraction study (crosses) [4] are also indicated.

TABLE II. Energy of metastable $O_kO_lT_mT_n$ configurations with different Li^+ fillings k , l and m , n in the two octahedral (O) and two tetrahedral (T) sites, respectively, considered in the DFT calculation. The two $O_3O_1T_2T_2$ configurations correspond to two inequivalent minima as explained in the text.

Configuration	Calculated Energy (eV)
$O_2O_2T_2T_2$	Ground State
$O_3O_1T_2T_2/1$	0.35
$O_3O_1T_2T_2/2$	0.47
$O_4O_0T_2T_2$	0.73
$O_4O_1T_1T_2$	1.04

0.02 eV/Å. The error in the values of Table II comes from several sources; apart from the approximation of DFT, the true energies of the metastable states will be somewhat lower due to further relaxation which was not possible in our calculation involving only 2 f.u. To quantify this, we computed the energy difference in one case using 256 atoms, and obtained a further relaxation of 0.15 eV. When one octahedral site was triply occupied and the other one was singly occupied, we found two different configurations corresponding to two local minima, with energies of 0.47 and 0.35 eV with respect to the global minimum configuration. When one octahedral site was quadruply occupied and the two Li^+ ions came from either the other octahedral site or from a tetrahedral and an octahedral site, the energies were 0.73 and 1.04 eV, respectively. These results show that in stoichiometric polymeric Li_4C_{60} there are unoccupied interstitial octahedral sites that can be filled by Li^+ cations. Configurations in which more than two cations occupy an octahedral site have low energies and can form at low temperatures and enable Li^+ diffusion in the lattice.

A diffusion pathway of suitable size is a further condition for ionic conductivity. A close inspection of the Li_4C_{60} structure shows that smaller tetrahedral voids interconnect the octahedral regions, as shown in the inset of Fig. 1. Here the pink/grey (medium grey/light grey) structure indicates the loci of the centers of a spherical probe, with a diameter equal to that of a Li^+ ion (ionic radius 0.7 Å), rolling over the van der Waals-accessible C_{60} surfaces. It is remarkable that the C_{60} two-dimensional polymerization does not hinder the ionic diffusion. Li^+ ion diffusion is not confined to planes between the polymer sheets, it takes place in a three dimensional network.

Our experimental results and the structural calculations show that in Li_4C_{60} Li^+ ions diffuse and give the main contribution to the electrical conductivity at frequencies below a few times 10^6 Hz and at temperatures between 130 K and the polymer-to-monomer transition temperature. As summarized in Table I, both NMR and ac conductivity measurements found a remarkably low activation

energy for the Li^+ ion diffusion, $E_a = 200$ meV, the value of 240 meV fitted for dc conductivity is only slightly larger.

There is a larger difference between the preexponential factors τ_0 (correlation time extrapolated to infinite temperature) measured by NMR and ac conductivity. The approximately 50 times larger τ_0 found in conductivity measurements is explained by considering that Li^+ jumps between the 4 allowed positions inside the octahedral sites contribute to the nuclear spin relaxation, while they are not relevant for the electrical conductivity, which depends only on the intersite jumps.

In conclusion, we found that Li_4C_{60} polymer is an almost ideal Debye superionic conductor with an extremely high ionic conductivity. This is made possible by the relatively low activation energy of Li ion diffusion, and the intrinsic interstitial sites, which are vacant at low temperatures but can be multiply occupied without a large energy expense. This opens the possibility for a new application of fullerides, intercalated with small size ions, in batteries.

We acknowledge financial support from the EC FP6-NEST Ferroc carbon project and the Hungarian State Grant OTKA NK60984.

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