## In-Plane Jump Diffusion of Li in LiC<sub>6</sub>

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Li diffusion in LiC<sub>6</sub> has been measured by high-resolution neutron spectroscopy both in the ordered phase between 630 and 675 K and in the disordered phase at 720 K. The in-plane diffusion constant D at 660 K is  $1 \times 10^{-6}$  cm<sup>2</sup>/s, which increases to  $24 \times 10^{-6}$  cm<sup>2</sup>/s above  $T_c$ . At all temperatures, a jump-type diffusion mechanism was observed, with jump vectors connecting nearest Lisublattice sites in the ordered phase, but nearest hexagon centers in the disordered phase.

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The planar diffusivity of alkali-metal atoms in graphite intercalation compounds (GIC's) has recently become the focus of much research activity. DiVincenzo and Mele<sup>1</sup> estimated the activation energies and selfdiffusion constants of alkali atoms in stage-1 GIC's using a Thomas-Fermi approach of the densityfunctional theory (by a stage-n compound we understand a periodic structure in which any successive intercalate layers are separated by n carbon basal planes). Quasielastic neutron-scattering experiments<sup>2,3</sup> have provided the first information on the planar alkalimetal diffusivity and the diffusion mechanism in a number of stage-1 and stage-2 compounds. These results have stimulated further NMR<sup>4</sup> and x-ray<sup>5</sup> work on the alkali-metal diffusion in GIC's. Although quasielastic neutron scattering (QENS) is one of the most powerful tools for the study of diffusion in solids,<sup>6,7</sup> the method can be applied most favorably to nuclei which exhibit a large incoherent scattering cross section for thermal neutrons. However, all heavy alkali-metal nuclei have predominantly coherent cross sections, in which case one cannot explore the diffusivity in the ordered state since the neutron intensity is then entirely concentrated in the Bragg peaks. The QENS method also breaks down in the disordered, liquidlike state for scattering vectors Q >> 1 Å<sup>-1</sup>, where long-range diffusion is observed (hydrodynamic limit).

In this Letter we report the first QENS study of <sup>7</sup>Li diffusion in the compound LiC<sub>6</sub>. The isotope <sup>7</sup>Li has an incoherent cross section for thermal neutron scattering of  $\sigma_{inc} = 0.7$  b, which is about equal to the coherent cross section.<sup>8</sup> It is thus the only alkali-metal isotope with an appreciable incoherent scattering cross section. Therefore, QENS studies of the Li diffusion

are possible in the ordered as well as in the disordered state above the Li-sublattice melting transition of 715  $K.^9$ 

 $LiC_6$  is unique among the alkali-metal GIC's in still another way. It has the smallest unit-cell volume with an in-plane  $\sqrt{3} \times \sqrt{3}R30^\circ$  Li sublattice and an  $A\alpha A\alpha$ layer-stacking sequence (A = graphite basal plane, $\alpha$  = intercalate layer) with a periodicity of 3.71 Å, only 10% larger than in pristine graphite.<sup>10</sup> Hence the electronic<sup>11</sup> and lattice-dynamical properties<sup>12</sup> of LiC<sub>6</sub> exhibit less anisotropy than those of the heavy alkalimetal compounds. Because of the strong binding the Li sublattice is well ordered, and the disordered phase also seems to be commensurate above  $T_c$ .<sup>9</sup> Thus, we expect the planar Li diffusivity to be much smaller than in the heavy alkali-metal GIC's and we also expect it to be closely related to the vacancy concentra-Furthermore, the layer-stacking sequence tion.  $A\alpha A\alpha$  provides open channels parallel to the hexagonal axis, suggestive of a possible one-dimensional diffusion of the Li<sup>+</sup> ions normal to the plane.

In this experiment we used 31 cm<sup>3</sup> of isotopeenriched <sup>7</sup>LiC<sub>6</sub>. The intercalation procedure and the stage fidelity are described in Ref. 3. For the present measurements the sample was transferred to a thinwalled, stainless-steel container with some excess <sup>7</sup>Li metal at the bottom separated from the sample by a perforated platform and shielded from the main beam by a Gd foil. The Li diffusion was measured both in the ordered phase between 630 and 675 K and in the disordered phase at 720 K. The experiments were performed at two spectrometers situated at the coldneutron guides of the Institut Laue Langevin: the QENS in the low-temperature phase was measured at the back-reflection spectrometer IN10 with an energy resolution of 1  $\mu$ eV (FWHM) and the hightemperature measurements were performed at the time-of-flight spectrometer IN5 with a resolution of 63  $\mu$ eV. (For further details about the spectrometers we refer the reader elsewhere.<sup>13</sup>)

After the measurements at the highest temperature of 725 K, optical inspection, neutron diffraction, and further QENS did not indicate any deterioration of the sample.

In the ordered phase of  $LiC_6$  the coherent-scattering contribution is almost entirely contained in the Bragg reflections and QENS is only expected from the incoherent part of the scattering function. Above the critical temperature the Li sublattice presumably forms a disordered lattice gas.<sup>9</sup> Since the lattice-gas structure factor exhibits Bragg reflections at the HK0 reciprocal lattice points of graphite and weak short-range-order diffuse scattering in between the Bragg reflections, the dominant scattering contribution away from Bragg reflections stems again from the incoherent part of  $S(Q, \omega)$ . With use of a lattice-gas model, an estimate of the ratio of the incoherent to the coherent scattering intensity between Bragg reflections yields a value of 4 to 5. Thus, above as well as below the transition temperature, the QENS from the <sup>7</sup>Li diffusion is dominated by incoherent scattering.

The measurements probing diffusion normal to the planes showed purely elastic scattering up to 675 K within our resolution of 1  $\mu$ eV, whereas QENS was observed from in-plane diffusion above 630 K. Therefore LiC<sub>6</sub>, like the heavy alkali atoms, exhibits twodimensional particle diffusion between the graphite basal planes. Any channel-like diffusion, if existing, must be much slower than the in-plane mobility. In the following we will discuss only the latter. A typical scattering function  $S(Q, \omega)$  at Q = 1.4 Å<sup>-1</sup> and T = 625 K is shown in Fig. 1(a). The solid line through the data points is obtained by fitting the data with a  $\delta$  function convoluted with the measured resolution function. This fit describes the data points very well and no additional Lorentzian-type broadening due to the diffusion is detectable. However, at the higher temperature of 675 K [Fig. 1(b)] the same fit can no longer completely describe the measured scattering function. But an excellent fit to the data points is obtained with the sum of a  $\delta$  function and a Lorentzian line shape, both convoluted with the resolution function. This additional Lorentzian linewidth is due to the diffusion of the Li atoms. The elastic or  $\delta$ -type scattering, which remains at higher temperatures, is probably due to diffuse scattering from the graphite host.

We have measured the scattering function  $S(Q, \omega)$ at several scattering vectors Q and analyzed the Q dependence of the energy width  $\Gamma$  of the Lorentzian component. This is shown for two different tempera-



FIG. 1. (a) Scattering function  $S(Q, \omega)$  of LiC<sub>6</sub> at 625 K and a wave vector Q = 1.4 Å<sup>-1</sup> parallel to the *HK*0 plane taken at the backscattering spectrometer IN10. Full line represents a best fit by a  $\delta$  function convoluted with the instrumental resolution function. (b) Same scattering function as in (a) only at 675 K. The full line again represents a fit by a  $\delta$  function convoluted with the instrumental resolution. The additional scattering in the wings is attributed to quasielastic scattering from planar Li diffusion.

tures above and below the Li-sublattice melting transition in Fig. 2. At 660 K [Fig. 2(a)]  $\Gamma$  increases first to a maximum of 4  $\mu$ eV at  $Q \approx 1$  Å<sup>-1</sup>, followed by a significant decrease at higher Q values. In contrast, at 720 K [Fig. 2(b)]  $\Gamma$  is still increasing even beyond Q=1 Å<sup>-1</sup> and has a maximum of 230  $\mu$ eV at about 1.5 Å<sup>-1</sup>. Note the instrumentally limited Q range of



FIG. 2. (a) Linewidths (FWHM) of quasielastic neutron spectra measured as a function of the wave-vector transfer to  $\text{LiC}_6$  at 660 K. These measurements were carried out at the backscattering spectrometer IN10; the inset shows a schematic outline of the  $\text{Li}-\sqrt{3} \times \sqrt{3}R 30^\circ$  superlattice.  $I_1$  and  $I_2$  designate possible jump vectors for diffusion. (b) Same as in (a) at 720 K, 5 K above the melting temperature of the Li sublattice. These measurements were taken at the time-of-flight spectrometer IN5.

these latter measurements carried out at IN5, as compared to the more extended Q range of IN10. Nevertheless, there is an oscillatory behavior or at least a saturation of the quasielastic linewidth  $\Gamma$  observable, contrary to what one would expect from a continuous liquidlike diffusion process. Thus the present data suggest a jumplike diffusion process in both the ordered and disordered phases.

The inset of Fig. 2(a) shows the hexagonal closepacked in-plane structure of the Li superlattice, decorating the hexagon centers of the graphite basal plane. Rapid diffusion in the ordered phase requires vacancies in the Li lattice, which certainly exist in our temperature range close to the sublattice melting transition, and which are evidenced by the temperature dependence of the superlattice reflection.<sup>9</sup> The structure LiC<sub>6</sub> suggests two possible jump vectors: either jumps to the nearest hexagon centers with a jump distance of  $l_1 = 2.46$  Å, or jumps within the Li sublattice, requiring a jump distance of  $l_2 = 4.26$  Å. In our pyrolytic graphite sample the jump vectors are directionally averaged, such that we can only determine their



FIG. 3. Arrhenius plot for the diffusion constant in the ordered phase of LiC<sub>6</sub>. The dashed line is a best fit to the data points with an activation energy of  $E_a = 1$  eV. The datum point above the dashed line indicates the diffusion constant at 720 K in the disordered phase.

lengths. To simulate the appropriate two-dimensional average, we have calculated the scattering function  $S(Q, \omega)$  according to the Chudley-Elliott model for jump diffusion<sup>14</sup> as a function of the angle between the scattering vector and the jump vector. The scattering functions are summed in small angular increments, normalized, and convoluted with the experimental resolution function. Finally, the result was treated with the same program as the experimental data, and a master curve was extracted for the quasielastic linewidth. For the jump distance  $l_2$  this curve, shown as a solid line in Fig. 2(a) for a diffusion constant  $D = 1 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>, reproduces the ordered-phase data rather well. At 720 K the increase of  $\Gamma$  between Q = 1 Å<sup>-1</sup> and 1.5 Å<sup>-1</sup> excludes the same diffusion mechanism for the disordered phase. The results of Ref. 9 suggest, however, a lattice-gas-type Li structure above  $T_c$ , in which case the data in Fig. 2(b) indicate a jump diffusion with reduced jump distance.

Indeed, a similar master curve with a jump distance  $l_1$ , shown as a solid line in Fig. 1(b) for a diffusion constant  $D = 24 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>, simulates the continuing increase of the linewidth beyond Q = 1 Å<sup>-1</sup> and the saturation around  $Q \approx 1.5$  Å<sup>-1</sup> quite well.

Figure 3 shows an Arrhenius plot of the diffusion constants measured at various temperatures in the ordered phase. In spite of the large error bars, these data reveal an activation energy of  $E_a \approx 1 \text{ eV}$ , which is considerably larger than the activation energy found in an earlier NMR study at lower temperatures.<sup>15</sup> However, the high activation energy obtained in the present study likely contains a significant contribution from the enthalpy of vacancy formation. Recently DiVin-

cenzo and Mele<sup>1</sup> calculated the activation energy  $E_a$  for stage-1 compounds, based on a density-functional approach. For Li diffusion they obtain a value of  $E_a = 1.3$  eV, which is much larger than for the heavy alkali-metal diffusion and which is in remarkably good agreement with our results.

In summary, we have measured for the first time the Li diffusion in LiC<sub>6</sub> in the ordered and disordered phases between 630 and 720 K by quasielastic neutron scattering. In both phases the data indicate a jumptype diffusion process. In the ordered phase below 715 K the jump vectors connect sites within the  $\sqrt{3} \times \sqrt{3}$  Li sublattice, while above the melting temperature the assumption of jumps to nearest-neighbor hexagon centers seems appropriate. At the same time the jump rate increases dramatically. In the ordered phase we find a surprisingly high activation energy of about 1 eV, which might contain contributions from the creation of vacancies in the temperature range of our measurement.

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