PHYSICAL REVIEW B VOLUME 40, NUMBER 16 1 DECEMBER 1989

Diffusion of lithium in highly oriented pyrolytic graphite at low concentrations and high temperatures

B. Jungblut and E. Hoinkis
Hahn-Meitner-Institut Berlin, C3, D-1000 Berlin 39, Federal Republic of Germany

(Received 30 May 1989; revised manuscript received 7 August 1989)

Graphite forms intercalates with a variety of elements and molecules because of the absence of chemical bonding between the hexagonal layer planes. The formation of stage-one intercalate LiC_6 increases the interlayer distance from 0.335 to 0.371 nm. Although the diffusion of Li into graphite precedes intercalate formation, no data exist for Li transport at low Li concentrations. The release kinetics of Li was measured from highly oriented pyrolytic graphite (HOPG) at Li concentrations between 1 and 10 ppm and temperatures in the range from 1000 to 1300 K, and diffusion coefficients for the isotopes ^7Li and ^6Li were determined. The Li transport in HOPG is strongly anisotropic, and the contribution to the total release of the diffusion perpendicular to the graphite planes is negligible. The Li diffusion coefficients in the direction of the graphite planes are given by $D=(3\times10^3\ \mathrm{cm^2/s})\exp(-1.83\ \mathrm{eV}/kT)$. The D value at 1070 K is $7.6\times10^{-6}\ \mathrm{cm^2/s}$.

INTRODUCTION

The system Li/graphite has attracted special interest because the graphite intercalation compounds (GIC's) of Li differ from the other alakaline GIC's in their structure and electronic properties.[1] Comparatively few works have been published on the Li diffusion in LiC_6 (Refs. 2–6), and we are not aware of data for the Li diffusion at Li concentrations below that of the GIC compounds. At very low Li concentrations methods such as quasielastic neutron spectroscopy (QNS) and nuclear magnetic resonance (NMR) are not successful due to the limited sensitivity. Also, traditional tracer methods cannot be utilized because the radioactive nuclides of Li have very short half-lifes. Moreover, depth profiling techniques, such as secondary ion mass spectroscopy (SIMS), do not seem to be applicable, since preferential sputtering results in a very rough surface with pronounced carbon cones.[7] Therefore one of us (E.H.) designed an experiment for measuring the isothermal release kinetics of Li from homogeneously Li-doped highly oriented pyrolytic graphite (HOPG) with the help of a mass spectrometer. The experimental procedure is described and diffusion data are presented for Li concentrations between 1 and 10 at. ppm. Strong evidence is given for a pronounced anisotropy of the Li diffusion in HOPG, and this is mainly in-plane transport. The activation energy in the concentration and temperature range (1000–1300 K) investigated is considerably larger than the values published for Li in LiC_6.[2–6]

SAMPLE PREPARATION

Highly oriented pyrolytic graphite (HOPG) is a polycrystalline graphite with a high degree of preferred orientation of the crystallites parallel to the basal planes, and has almost the theoretical density ($\rho_{\mathrm{HOPG}}=2.26\ \mathrm{g/cm^3}$). We used the HOPG grade ZYD (mosaic spread: 1.2°) produced by Union Carbide. HOPG does not have accessible pores.

The HOPG samples were cut from a plate using a laser. All specimens were cylinders with either 5 or 7 mm diameter. Their height varied between 0.36 and 0.76 mm. The basal planes were perpendicular to the cylinder axis (*c*-axis parallel to the cylinder axis).

Contamination possibly introduced during the preparation of the samples was reduced by annealing all specimens in a spectroscopic grade graphite crucible at 1300 K under high-vacuum conditions ($<10^{-6}$ mbar) for at least 24 h. The HOPG specimens were loaded into a cylindrical glassy carbon container together with Poco graphite spheres, which had been annealed, impregnated with a saturated solution of Li_2CO_3 in water, and dried previously. Poco graphite is a highly purified, macroscopically isotropic graphite with an open porosity of 16%. The graphite grains are nearly perfect, and no binder is used in the production process. The glassy carbon container was sealed by a tightly fitting lid also made of glassy carbon. This container was then placed into a tantalum capsule. After evacuating, the tantalum capsule was sealed by electron beam welding and then annealed at 1300 K in a high vacuum for periods of time between several hours and two weeks, which is sufficient for reducing the Li_2CO_3 in the Poco spheres to Li ($Li_2CO_3 \rightarrow Li_2O+CO_2$, $Li_2O+C \rightarrow 2Li+CO$) and for distributing the Li homogeneously in both graphites, Poco and HOPG. The obtained Li-doped HOPG samples were then transferred to the ultrahigh vacuum (UHV) system in which the release measurements were performed.

From published data of the Li decomposition pressures of Li_2C_2 as a function of temperature[8] it is unlikely that Li carbide is formed, because the Li amounts applied during the doping procedure are very low. However, the results reported in Ref. 8, and in the references therein may not be fully convincing because the enthalpy of formation data spread widely. So, in order to verify the absence of a significant amount of Li_2C_2, a test was performed as follows. A Poco graphite sample with a Li content of 3.6 ppm Li was ground in a glove box containing purified Ar

($O_2 < 1$ ppm, $H_2O < 0.1$ ppm). The obtained powder was filled into a vessel sealed with a septum. After injection of H_2O, a sample of the gas phase was analyzed using a gas chromatograph (HP 5890) equipped with a Al_2O_3/KCl coated capillary column and a flame ionization detector. The amount of C_2H_2 evolved due to the reaction $Li_2C_2+2H_2O \rightarrow 2LiOH+C_2H_2$ was not measurable. The C_2H_2 detection limit of the gas chromatograph was determined, and calibration measurements were performed. From the C_2H_2 detection limit it was calculated that the corresponding Li amount bonded as Li_2C_2 in the specimen must be less than 2% of the total Li content and therefore negligible (the solubility of C_2H_2 in H_2O was taken into account). In accordance with a phase diagram published by Woo *et al.*,[9] we therefore assume that a disordered stage one Li intercalate of very low Li density and no long-range order with respect to Li is formed in the doping procedure. This phase is to be understood as a strongly diluted solution of Li in graphite.

An electron-probe x-ray microanalysis (EPXMA) of the inner surface of the glassy carbon container demonstrated that a significant amount of Ta had not penetrated the glassy carbon seal.

EXPERIMENTAL

The release experiments were performed under ultrahigh-vacuum (UHV) conditions, and the base pressure of the system is better than 3×10^{-10} mbar. The experimental setup is drawn schematically in Fig. 1 and consists of three main components: furnace (labeled 1), chopper (labeled 8), and mass spectrometer (labeled 10).

The specimen is heated in a tantalum crucible (labeled 2), which has an electropolished tungsten liner (not shown). The crucible is heated resistively by means of a sheethed tantalum wire (labeled 3). A number of shields (labeled 4) reduce radiation losses, and the furnace housing is water cooled. The temperature of the crucible is measured by a Pt-RhPt thermocouple (labeled 5), and is kept constant to within 2 K by a suitable controller. A sample (labeled 6) can be dropped into the crucible by means of a manipulator with pincer grip head (labeled 7). The chopper (Bulova, L40HH) is built into a separate housing also cooled by water. The quadrupole mass spectrometer (Extranuclear, 270-9; electron impact ionizer) and the furnace are fitted to the chamber by bellows which allow adjustment. A channeltron multiplier (Galileo, 4810) is used for detection of the mass-selected ions.

The furnace and the mass spectrometer (MS) are pumped differentially by Varian Star Cell ion pumps. A valve fitted to the MS housing allows the MS to be left operating while the UHV chamber is being flooded for sample exchange. This ensures the constant operating conditions of the MS.

The sample temperature is measured by means of a

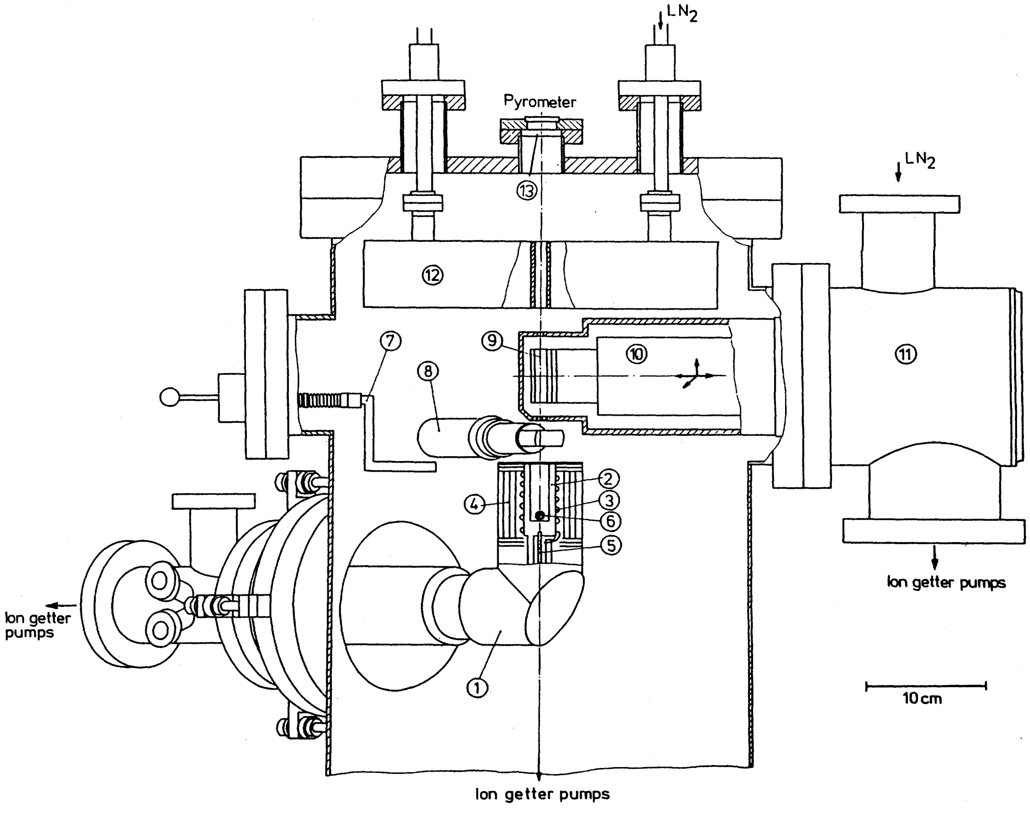

FIG. 1. Experimental setup of the release experiment. For details see the text.

calibrated optical micropyrometer (Pyro Werk, PB06). The specimen may be observed directly through the apertures in the housings of the MS and the chopper and through an additional aperture in the cold wall (labeled 12) and a viewport (labeled 13). Inside the crucible an area of about 8 mm^2 can be seen, which is also the effective area "seen" by the MS. To measure the temperature, the chopper has to be drawn out of the beam line.

The chopper and the MS are controlled by a digital MS processor designed at the Hahn-Meitner Institute (HMI). Three modes are possible: (i) recording of mass spectra, (ii) measurement of ionization yield curves at constant mass by variation of the electron energy of the ionizer (4–100 eV), and (iii) measurement of the time dependency of the ion intensities for up to five masses. The latter ion counting mode was used for measuring the release kinetics of the naturally occurring isotopes ^{6}Li and ^{7}Li. The data obtained using any of these modes are transferred to an HP series 80 computer system for evaluation.

The fractional release $F(t)$ was calculated from the measured release rate $m(t)$ in the following way. $F(t)$ is defined as

$$F(t)=[l(t=0)-l(t)]/l(t=0)\ , \tag{1}$$

where l is the Li quantity within the specimen. The integration over the release rate $m(t)$ is proportional to the quantity released,

$$l(t=0)-l(t)=K\int_0^t m(t')dt'\ , \tag{2}$$

and therefore

$$F(t)=\int_0^t m(t')dt' \Big/ \int_0^\infty m(t')dt'\ . \tag{3}$$

The total Li quantity present in the specimen at $t=0$ was obtained from $\int_0^\infty m(t')dt'$ and the constant K. One notes that the fractional release data $F(t)$ are independent of the constant K. For a quantitative determination of the Li content of the specimens at $t=0$ the constant K was determined in separate experiments (see the following).

A problem with the measurement of very low Li^+ signals arises from C^{2+} and N^{2+} ions contributing to the intensities of the masses 6 and 7 u. Reduction of the electron energy of the impact ionizer from normally 100 to 20 eV is sufficient to produce mainly $^6Li^+$ and $^7Li^+$ ions. At the end of the release experiments background count rates less than 2 cps were measured and, therefore, no background correction of the release rate functions had to be performed in most cases. No evidence was found for the occurrence of Li_nO^+ or Li_nC^+ species. Whereas Wu *et al.*[10] detected Li_3C^+ and Li_4C^+ ions in a permeation experiment with a probably much higher Li concentration, Asano *et al.*[8] only detected Li^+.

It is obviously important for the samples to be heated up in a time which is small compared to the isothermal release time. The sample heat up was measured by dropping a Poco graphite sample (sphere, 5-mm diameter) equipped with a sheethed thermocouple (0.5-mm diameter) into the preheated crucible at four temperatures within the range of the measurements. In all cases the temperature 10 K below the steady state temperature was obtained within 120 s or less. Such an experiment is not possible with HOPG, since it is difficult to insert a thermocouple in HOPG specimens, which have a thickness less than 1 mm. However, the HOPG samples are expected to heat up faster than a 5-mm Poco sphere due to their smaller volume.

In order to check whether interactions of Li and tungsten disturb the release measurements, a Li-doped graphite sample was dipped into the preheated crucible (1163 K) and removed again as soon as a strong Li signal had been measured. The Li signal dropped below the 10% level in 17 s after the sample had been removed, and it is evident that the desorption rate of Li from the electropolished tungsten is much faster than the diffusion rate of Li in graphite at the same temperature (see the section labeled Results and Discussion).

The calibration with respect to Li quantities of the experimental setup was performed using reference measurements with graphite permeation cells. The cells consist of Poco graphite cylinders 5 mm in diameter and 8 mm high. A 2-mm hole was drilled along the cylinder axis to a depth of 5 mm. This hole was closed by a Poco graphite stopper after Li_2CO_3 solutions with different concentrations had been put into the holes of separate graphite cylinders. The amounts of Li were in the range from 6 ng to 6 μg Li. The permeation cells were dried, and subsequently the total Li release from the cells was measured. At a crucible temperature of about 800 K reduction of the Li_2CO_3 began (the cells were dropped into the cold crucible), indicated by a pressure rise and by an increase in the CO (and H_2O) signals (CO_2 could not be detected because of the chosen limited mass range of the mass spectrometer). The reaction seemed to be completed within one minute without any Li release until then. At a crucible temperature around 1100 K the Li signals appeared and were followed until they had decreased below the detection limit again. The total count numbers for $^6Li^+$ and $^7Li^+$ were calculated by integration of the count rates. The ratio of the count numbers of the isotopes $^7Li/^6Li$ was 12.2 ± 0.1 for all four experiments (the isotope ratio according to the natural abundance is 12.477). A count number of 7.8×10^5 counts corresponds to 1 μg Li.

RESULTS AND DISCUSSION

HOPG is highly anisotropic with respect to its physical properties. It was therefore investigated first to find out whether the Li diffusivity is anisotropic as well. Figure 2 shows a diffusion measurement performed with a sample with its basal planes oriented parallel to the beam axis of the experimental setup (see Fig. 1) and having been dipped into the crucible ($\|$). An additional measurement (similar sample temperature) was plotted, in which the sample orientation was perpendicular to the above ($\perp$). In the latter case only a very small peak, probably due to the desorption of Li from the basal plane surface, can be seen. In order to verify this result a device was designed which allowed a HOPG sample to be rotated *"in situ"* around an axis perpendicular to the basal planes. The result of an experiment performed using this rotation de-

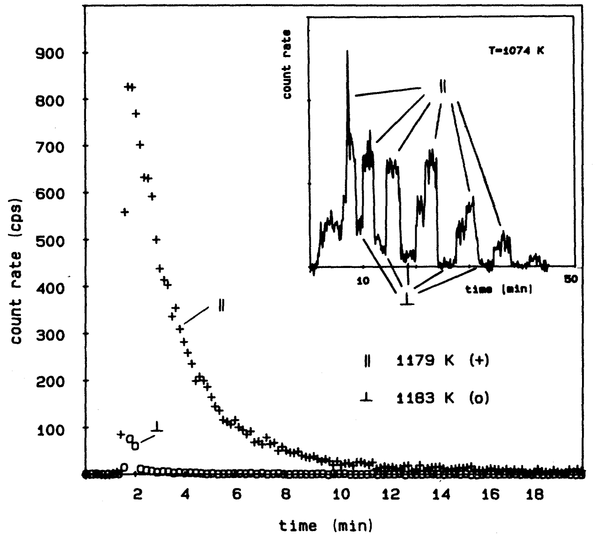

FIG. 2. Comparison of the Li amounts released parallel (||) and perpendicular (⊥) to the basal planes. Inset: "*in situ*" rotation of a HOPG sample during measurement. The steps occur within seconds.

vice is shown in the inset of Fig. 2. The high count rates correspond to the basal planes being parallel to the beam axis (||) and low count rates to the basal planes being perpendicular to the beam axis (⊥). In both positions the rates were sensitive to small deviations from 0° and 90°. In total, Fig. 2 indicates that a larger amount of Li is released in the direction of the basal planes if compared to the perpendicular orientation (a factor of approximately 80 is estimated from Fig. 2). It must be concluded that the coefficient for Li diffusion in HOPG in the direction perpendicular to the basal planes (*c*-axis direction) is by far lower than parallel to the planes. Thus, grain boundary diffusion and diffusion through vacancies in the graphite planes seem to be negligible. It is likely that the results presented above even underestimate the anisotropy of the Li diffusivity, because HOPG crystallites are not orientated perfectly, as can be seen from the mosaic spread of 1.2°. In addition, some of the Li atoms which desorb from the basal plane face of the specimen may have arrived there via surface diffusion from the edge of the specimen (Li is known to adsorb on the basal planes[11]). All HOPG diffusion experiments reported later were performed with the basal planes parallel to the MS viewing direction.

Data for the diffusion of Li exist only for the stage one intercalation compound LiC_6. The QNS investigation by Magerl *et al.*[4] shows that the transport perpendicular to the planes, "if existing, must be much slower than the in-plane mobility." Li diffusion perpendicular to the planes in graphite at very low Li concentrations is then very unlikely, because the channels existing in LiC_6 ($A\alpha A\alpha\cdots$ stacking), which could be possible jump paths, are not present in graphite ($ABAB\cdots$ stacking). This work presents evidence for the strong anisotropy of the Li diffusion in graphite (Li concentration below intercalate formation) for the first time using a "classical" method. Because of this strong anisotropy, a diffusion equation for two-dimensional diffusion was applied to the measured HOPG release data, and Li diffusion in the *c*-direction was neglected.

The solution of Fick's second law $\partial c/\partial t = \mathrm{div\ grad}\ c$ for diffusion in a cylinder in radial direction only with

$$c = c_0 \text{ for } 0 < r < R \text{ and } t = 0\ , \tag{4}$$

$$c = 0 \text{ for } r = R \text{ and } t \geq 0 \tag{5}$$

is

$$F(t) = 1 - \sum_{n=1}^{\infty} \frac{4}{\xi_n^2} \exp(-\xi_n^2 Dt/R^2)\ . \tag{6}$$

$F(t)$ is the fractional release, D the diffusion coefficient, R the cylinder radius, and t the time variable. ξ_n are roots of the equation $J_0(x)=0$, wherein $J_0(x)$ is the Bessel function of order zero. The fractional release is dependent on a dimensionless variable α^2, which is defined as

$$\alpha^2 = Dt/R^2\ . \tag{7}$$

So, $\alpha^2(t)$ may be calculated from the $F(t)$ data, and a plot of α^2 versus t should give a straight line through the origin, provided that, first, the above assumptions are met, and, second, the process can be described by Fick's second law. For some experiments theoretical release rates were calculated numerically and compared with the measured data.

Figure 3 shows two examples of α^2 plots for different temperatures. The curve obtained at 1085 K corresponds to the 60 min time scale and the experiment at 1254 K to the 6 min scale. From Fig. 3 it can be seen that the α^2 plots are linear for fractional release values from about 20% to 90%. In general, all experiments reveal release values at low fractional releases which are too low if compared to theory and lead to the *t*-axis intercepts being

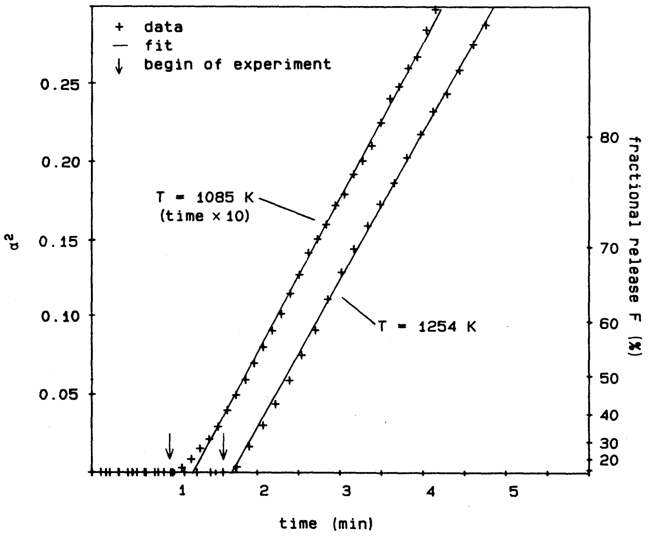

FIG. 3. Plots of $\alpha^2(t)$ for Li in HOPG according to Eq. (6) for radial diffusion only in cylinders.

larger than the starting time of the experiment. This is demonstrated in Fig. 4 by a comparison of experimental rates with a theoretical curve (no free parameters were used for calculating the theoretical curve). Immediately after the sample has been dropped into the furnace, the rates are lower than expected from theory. However, the agreement of experiment and theory assuming radial diffusion only is very good, if these first few data points are disregarded, and this initial deviation must be caused by a heating effect. The release of Li already begins at lower temperatures, leading to a depletion of Li in the near surface region of the sample. The sharp rate jump predicted by theory after the start of the experiment is smeared out by this, and causes the observed low initial release rates. Nevertheless, reliable D values can be obtained by evaluating the linear part of the α^2 plots as demonstrated by Gaus in theoretical work.[12]

Deviations from the theory at high release values ($F > 85\%$) are mainly due to the counting statistics of the measurements, and may occur for very low Li concentrations. Experiments performed with samples having a relatively high Li concentration result in better count statistics and, commonly, the α^2 plots are linear up to 95% release and beyond.

The diffusion coefficients measured for ^{7}Li in HOPG, at several temperatures and concentrations, are displayed in the Arrhenius plot, Fig. 5. Additionally, ^{6}Li diffusion coefficients were calculated from the release data obtained for the HOPG samples with approximately 10 ppm ^{7}Li content. The data marked by arrows are measurements carried out with cylinders with 7 mm diameter instead of 5 mm. From this figure it is apparent that (i) the values obtained are independent of diameter and height, (ii) no distinct isotope effect is observed, and (iii) no concentration effect is evident. The Li diffusion coefficients in HOPG are given by $D = (3\times 10^3\ \mathrm{cm^2/s})\exp(-1.83\ \mathrm{eV/kT})$. The error of $\log_{10}(D_0)$ was calculated to be 0.41, and the statistical accuracy of the activation energy is within ± 0.1 eV.

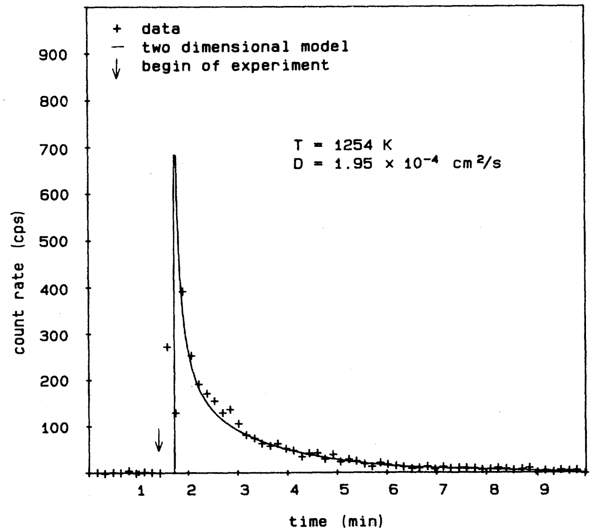

FIG. 4. Comparison of experimental release rate data (+) with the theory (solid line). The solution Eq. (6) was applied.

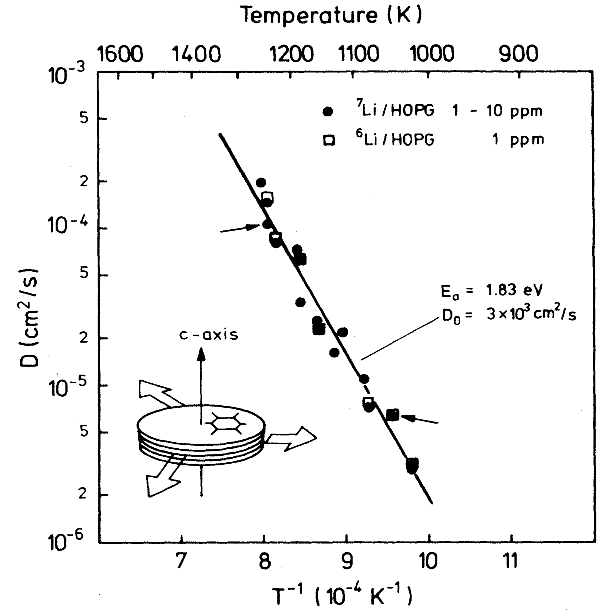

FIG. 5. Diffusion coefficients (symbols) and least-square fit (solid line) for Li/HOPG. The arrows mark experiments with cylinders 7 mm in diameter instead of 5 mm.

The fact that the values obtained with different sample radii are consistent had to be expected. The finding that the diffusion data are independent of the varying cylinder heights supports the two-dimensional diffusion model Eq. (6) proposed for Li in HOPG.

In the temperature range under investigation the lack of an isotope effect is not surprising. Such effects are liable to vanish at high temperatures. It is not surprising either that the D values are independent of concentration variations in the lower ppm range, because jump correlations or blocking effects are only to be expected at concentrations of about 1000 ppm or more.

The value of 1.83 eV, obtained for the activation energy, is significantly higher than 1 eV measured for the Li diffusion in $\mathrm{LiC_6}$ using QNS.[4] It is suggested that this discrepancy is mainly due to the Li concentration being by far lower than in $\mathrm{LiC_6}$. At such low Li concentrations it is of interest how the Li atoms influence the interlayer spacing of the host graphite lattice. Fisher *et al.*[13] measured the concentration dependence of the interlayer spacing in a substoichiometric $\mathrm{Li_xC_6}$ $(0.1 \le x \le 1)$, and demonstrated by comparison with theory that the rigid layer model is unlikely to be valid for this system. From their data they estimated the healing length of the graphite lattice distortion produced by an isolated Li atom to be 0.5 nm only. The distortion has a local character. This means that at very low Li concentrations the interlayer spacing is probably equal to graphite except in the close vicinity of the isolated Li atoms. Moreover, the graphite layer distance at an occupied Li site is probably less than that in $\mathrm{LiC_6}$. A correlation of the layer spacing and the activation energy of diffusion is given by theoretical calculations performed by Di Vincenzo *et al.*[3] for several stage-one alkali-metal intercalation compounds (Thomas-Fermi density-functional theory). For LiC_6 an activation energy of 1.3 eV was predicted, and the results for KC_8, RbC_8, and CsC_8 spread from 0.14 to 0.18 eV. The corresponding layer spacing is 0.371 nm for LiC_6, whereas the values for KC_8, RbC_8, and CsC_8 are between 0.535 and 0.593 nm. The activation energy obviously increases with decreasing interlayer distance. From this point of view it is consistent that the activation energy at ppm Li concentrations is significantly larger than reported by Magerl *et al.*[4] for LiC_6. In comparison to LiC_6, at low Li concentrations substantially more energy is required to move a Li atom within the interplanar space to an empty neighboring site. In LiC_6 (Li site distance: 0.426 nm) the host lattice is already expanded in the *c* direction by the Li atoms surrounding a Li vacancy.

Activation energies for Li in LiC_6 have also been estimated by NMR (Ref. 2) and β NMR,[5] yielding results of 0.2 and 0.6 eV, respectively, but these values are rather uncertain, because the evaluations have turned out to be very difficult for intercalation compounds. Moreover, the theoretical value of about 0.2 eV for LiC_6, calculated from a lattice simulation investigation by Morton-Blake *et al.*,[6] is probably also too low because, as the authors state themselves, the Li-C potential is not accurately known.

The very high D_0 values of 3×10^3 cm^2/s for Li/HOPG might be due either to long jump distances or to high-frequency factors. From Ref. 4 a value of about 10^2 cm^2/s can be estimated for Li in LiC_6. Frequency factors can be measured by adsorption and desorption experiments with Li atom beams. In the case of Li/graphite, Li atom beam experiments performed on basal plane surfaces should be successful because no considerable diffusion of adsorbed Li into the HOPG sample will take place.

The diffusion coefficients for Li concentrations in the ppm range should be helpful for the understanding of the formation of the intercalates. The finding that the D values of Li in HOPG are low if compared to the values published by Magerl *et al.*[4] for Li in LiC_6 (1×10^{-6} cm^2/s at 660 K) reveals the importance of the diffusion mechanism for initiating the intercalation. It is expected that the diffusion coefficient becomes strongly concentration dependent for Li concentrations at which high-stage intercalates are formed. Also effects caused by phase transitions (stages, order/disorder) become likely. First evidence for the influence of order/disorder transitions is given in Ref. 4 for Li in LiC_6.

ACKNOWLEDGMENTS

The authors wish to thank V. W. Gutsch (HMI, Bereich Datenverarbeitung und Elektronik) for designing the MS control unit and K. Adamski (HMI, Bereich Technik) for his help in the layout of the apparatus, which was built at HMI. The authors are indebted to H. Migge for valuable discussions and to Ch. Fischer for the C_2H_2 analysis.

---

[1] M. S. Dresselhaus and G. Dresselhaus, Adv. Phys. **30**, 139 (1981).

[2] J. Conrad and H. Estrade, Mater. Sci. Eng. **31**, 173 (1977).

[3] D. P. DiVincenzo and E. J. Mele, Phys. Rev. Lett. **53**, 52 (1984).

[4] A. Magerl, H. Zabel, and I. S. Anderson, Phys. Rev. Lett. **55**, 222 (1985).

[5] P. Freiländer *et al.*, Z. Phys. Chem. NF **151**, 93 (1987).

[6] D. A. Morton-Blake, J. Corish, and F. Beniere, Phys. Rev. B **37**, 4180 (1988).

[7] H. Gaus, W. Hensel, E. Hoinkis, and D. Stritzke, Hahn-Meitner-Institut Berlin, Report No. HMI-B 315, 1979 (unpublished).

[8] M. Asano, K. Kuho, and H. Kimura, J. Nucl. Mater. **102**, 353 (1981).

[9] K. C. Woo *et al.*, Phys. Rev. B **27**, 7831 (1983).

[10] C. H. Wu and H. R. Ihle, Chem. Phys. Lett. **61**, 54 (1979).

[11] Z. P. Hu and A. Ignatiev, Phys. Rev. B **30**, 4856 (1984).

[12] H. Gaus, Z. Naturforsch. **16a**, 1130 (1961).

[13] J. E. Fischer and H. J. Kim, Phys. Rev. B **35**, 3295 (1987).