Alkali-Metal Diffusion in Ternary Graphite Intercalation Compounds

by

P. C. Chow and H. Zabel
Department of Physics and Materials Research Laboratory
University of Illinois at Urbana-Champaign
1110 W. Green Street
Urbana, IL 61801

Introduction

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[1] calculated from a Thomas-Fermi approach of the density functional theory the activation energies and self diffusion constants of alkali-metal atoms in stage 1 GIC's. Quasi-elastic neutron scattering experiments[2-4] have provided the first information on the planar alkali-metal diffusivity and the diffusion mechanism in a number of stage 1 and stage 2 compounds. Although quasi-elastic neutron scattering is one of the most powerful tools to study diffusion in solids, the method can be applied most favorably to nuclei which exhibit a large incoherent scattering cross-section. However, all heavy alkali-metal nuclei have a predominantly coherent cross-section. In this case, the diffusivity in the ordered state cannot be explored.

In the following we describe an x-ray experiment which evades the difficulties of the neutron scattering technique and which allows us to determine the diffusion constant also in the ordered state. This method makes use of the substitutional intercalation of atoms M and M' (here M=Rb, M'=K) under well defined boundary conditions. The actual composition is determined locally via the shift of the (00ℓ) Bragg-reflections as a function of time.

Experimental

In the present experiment we used a square piece of HOPG (6.8 x 7.6 x .5 mm^3), which was initially intercalated to a pure stage 1 Rb-GIC. Following a procedure described earlier[5], we then opened the glass tube, removed the remaining Rb-metal and replaced it by K-metal. The vacuum sealed tube was then placed in a vertical two-zone x-ray furnace with independent control of the sample and alkali-metal temperature, which were set to T_S=250°C and T_K=152°C, respectively. In the glass tube was enough excess alkali-metal to insure constant alkali vapor pressure throughout the diffusion experiment. By in-situ (00ℓ) x-ray scattering we then measured the substitutional intercalation by monitoring the change of the c-axis repeat distance at the center of the sample (Fig. 1). MoK$_\alpha$-radiation in point focus geometry and monochromated by a graphite (002) reflection was used. The beam was collimated to a diameter of 2.5 mm at the sample position.

Results and Discussion

From previous data on the composition dependence of the layer spacing in the ternary $K_{1-x}Rb_xC_8$ compound[5] together with the present diffusion experiment we obtain the potassium concentration at the center of the sample as a function of time. The diffusion constant D can be determined from Fick's second law for the potassium composition X=X(x,y,t) in two dimensions

$$\frac{\partial X}{\partial t} = D\left(\frac{\partial^2 X}{\partial x^2} + \frac{\partial^2 X}{\partial y^2}\right), \qquad (1)$$

with the boundary condition for all times t:

$$X(\ell,y) = X(x,\ell) = X_o$$
$$\left.\frac{\partial X}{\partial x}\right|_{x=0} = \left.\frac{\partial X}{\partial y}\right|_{y=0} = 0 \qquad (2)$$

and the initial condition:

$$X(x,y,0) = 0 \qquad (3)$$

for $0 < x < \ell$ and $0 < y < \ell$. For the concentration at the center x=y=0 we find the solution

$$\frac{X(0,0,t)}{X_o} = \left[1-\left(\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}\right.\right.$$
$$\left.\left.\exp\left(-\left(\frac{2n+1}{2}\right)^2\pi^2\frac{Dt}{\ell^2}\right)\right)^2\right], \qquad (4)$$

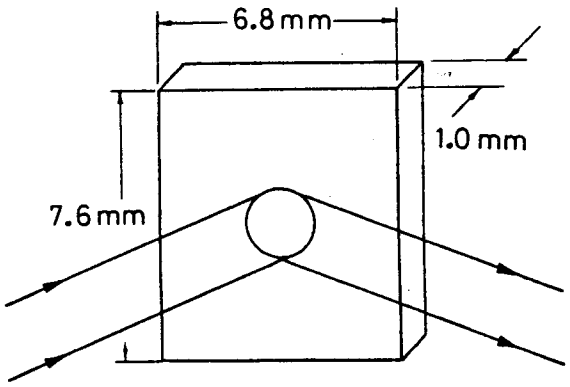

Fig. 1. Geometry of x-ray diffraction experiment for the study of the alkali-metal diffusion in stage 1 $K_{1-x}R_xC_8$ graphite intercalation compound. The (00ℓ) reflections were measured at the center of a square piece of the compound.

where X_0 is determined by the external K-vapor pressure. From preliminary data we obtain a diffusion constant of 2.6×10^{-7} cm^2/sec at 250°C. Since the diffusion process requires the Rb-atoms to migrate out of the sample at the same time as they are substitutionally replaced by K-atoms, the observed diffusion constant represents an average of the Rb and K-diffusion constants. Also, the activation energy for the jump-process, presumably via a vacancy mechanism, may contain an elastic energy contribution from the strain field around the substitutional defect, and this term will be composition dependent, since the interplanar spacing of the ternary compound deviates strongly from Vegard's law[5]. However, we estimate the elastic energy to be on the order of 10^{-2} eV and can therefore safely be neglected.

From quasi-elastic neutron scattering experiments close to the K-sublattice melting temperature[3], a prefactor $D_0=5.3\times10^{-4}$ cm^2/sec and an activation energy of Q = .144 eV have been obtained. The calculated diffusion constant at 250°C is then 2.2×10^{-5} cm^2/sec which deviates drastically from the value 2.6×10^{-7} cm^2/sec observed here. The discrepancy may be explained by a strong deviation from the Arrhenius behavior close to T_c, an effect which has also been observed in LiC_6[4]. In such a case, the above mentioned extrapolation is certainly not valid.

In conclusion, we have measured the diffusion of alkali atoms in the ternary compound $K_{1-x}Rb_xC_8$ by in-situ x-ray diffraction and have obtained a diffusion constant which is by two orders of magnitudes lower than the one which we estimate from previous quasi-elastic neutron work.

Acknowledgement

This work was supported by NSF DMR83-04890.

References

1. D. P. DiVincenzo and E. J. Mele, Phys. Rev. Lett. 53, 52 (1984), and to be published.

2. H. Zabel, A. Magerl, A. J. Dianoux, and J. J. Rush, Phys. Rev. Lett. 50, 2094 (1983).

3. H. Zabel, Extended Abstract, Materials Research Symposium on Intercalated Graphite, Boston (1984) edited by P. C. Eklund, M. S. Dresselhaus, and G. Dresselhaus, p. 6.

4. A. Magerl, H. Zabel, and I. S. Anderson, to be published.

5. P. C. Chow and H. Zabel, Synthetic Metals 7, 243 (1983).