Planar Diffusive Motion of Alkali-Metal Intercalant Atoms in Graphite

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The planar diffusive motion of alkali-metal atoms in the disordered phases of the compounds RbC_{24} and CsC_{24} has been studied for the first time by quasielastic neutron scattering. All neutron spectra show Lorentzian line profiles arising from liquidlike alkali-metal diffusion within graphite planes. The widths increase with temperature and show de Gennes narrowing at the peak of the intercalant structure factor. The results also show that Cs atoms diffuse faster than Rb atoms.

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X-ray analysis[1-6] of the alkali-metal structure factor in alkali-metal graphite intercalation compounds (AGIC's) revealed two-dimensionally (2D) short-range-ordered alkali-metal structures in the high-temperature phases of stage $n \geqslant 2$ compounds (n designates the number of graphite planes between any two consecutive alkali-metal layers). Although the question of commensurability of the alkali-metal layers with respect to the graphite basal planes is still controversial, there is no doubt that a lattice-gas-type disorder is inadequate to describe the structure factors.[4,7] The focus of interest here is whether this structure factor reflects an amorphous or rather "liquidlike" behavior for the dynamics of the alkali-metal subsystem. We have undertaken a quasielastic neutron scattering study on RbC_{24} and CsC_{24} to determine for the first time the energy width of the alkali-metal in-plane structure factor in AGIC's as a function of scattering vector and sample temperature. Since comprehensive data exist on the quasielastic linewidth of 3D liquid Rb,[8,9] a comparison promises to reveal important effects with regard to the dimensionality of the system.

Quasielastic spectra were recorded at the time-of-flight spectrometer IN6 at the high-flux reactor of the Institut Laue Langevin, Grenoble. The wavelength of the incoming beam was $\lambda = 5.1$ Å, yielding a resolution of about 100 μeV. The wave-vector transfer Q covered the region up to 2 Å^{-1}. The samples were prepared with the use of pyrolytic graphite with an initial mosaic spread of about 6-7°. After intercalation, the samples with cylindrical shape of diameter 22 mm and height 45 mm were taken out of their glass container and transferred into thin-walled Al sample chambers inside of a high-purity glovebox. The samples were mounted in a furnace so that the scattering plane was parallel to the graphite layers. Quasielastic spectra were taken from pristine graphite, RbC_{24}, and CsC_{24} between 280 and 620 K. The purity of the stage was established by neutron $(00l)$ scans before and after the quasielastic experiment. No deterioration of the samples after the heat treatment could be detected.

The resolution was determined by a dilute (4%) vanadium scatterer in place of the samples. Prior to fitting, the weak scattering from the Al sample container and the instrumental background were subtracted from all data.

Weak elastic diffuse scattering was observed for the pristine graphite sample as well as in the spectra of the intercalated samples at all temperatures. We attribute this scattering to the graphite substrate. We have not attempted to subtract this elastic contribution since it may be sample specific.

The results of these measurements are given in Figs. 1 and 2. Figure 1 (inset) shows a representative example of the scattering function $S(Q, \omega)$ for RbC_{24} at 343 K and $Q = 1.25$ Å^{-1}, derived from the time-of-flight data. The scat-

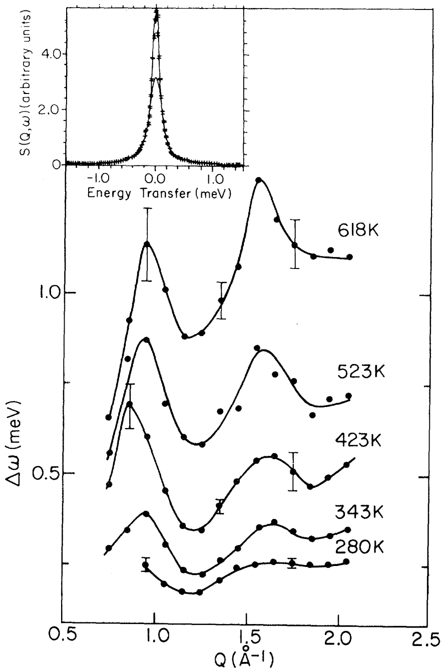

FIG. 1. Energy widths of the Lorentzian component of the scattering law $S(Q,\omega)$ with dependence on the scattering vector Q and for several temperatures, measured at the stage-2 compound RbC_{24}. Full lines are guides to the eye. The inset shows a typical quasielastic spectrum for RbC_{24} (shown by crosses) taken at $Q = 1.25$ Å and at 343 K. The solid line through the data points shows a fit with a δ function and a Lorentzian line shape, both convoluted with the instrumental resolution. The lower line shows the dominant contribution of the energy-broadened scattering.

tering function is well described by the sum of a δ function and a Lorentzian line shape, both convoluted with the instrumental resolution. The quality of the fit is shown in the inset of Fig. 1 by a solid line through the data points (crosses). The lower solid line represents the Lorentzian part of the spectrum. The dominant contribution to the scattering is contained in the Lorentzian or quasielastic component, whose energy width originates from the Rb diffusion within the intercalant plane. We attribute the δ-type contribution to a partially amorphous graphite substrate, as already mentioned above. In the following we will focus on the Lorentzian or quasielastic component of the spectrum only.

Three observations provide evidence that the quasielastic line broadening is due to alkali-metal in-plane mobility: (i) The widths of the spectra (full width at half maximum) at any wave vector Q increase with increasing temperature (Fig. 1). (ii) The Q dependence of the linewidths exhibits de Gennes narrowing.[10] (iii) This narrowing coincides with the maximum of the alkali-metal structure factor $S(Q)$ (Fig. 2). The de Gennes oscillations

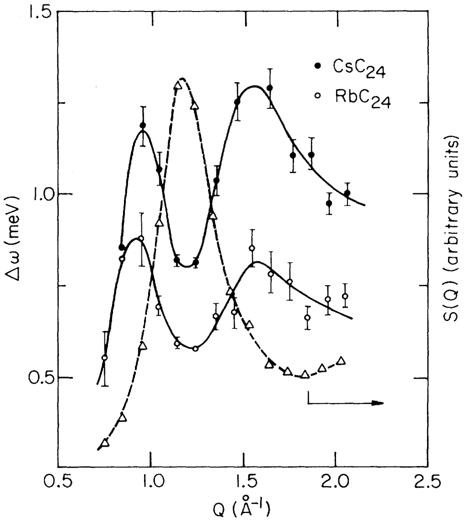

FIG. 2. Lorentzian linewidths for Cs and Rb diffusion in stage-2 graphite intercalation compounds at 523 K. The triangles indicate the structure factor $S(Q)$ for RbC_{24} at 523 as obtained by integrating $S(Q,\omega)$ with respect to ω. The full and dashed lines are guides to the eye.

$$\Delta\omega = 2DQ^2/S(Q) \tag{1}$$

are required by the second moment of the coherent scattering law, yielding quasielastic linewidths which exhibit minima at positions of Q for which $S(Q)$ has maxima. (D is the diffusion constant.) The physical basis for the de Gennes narrowing is that peaks in the structure factor $S(Q)$ occur at wave vectors corresponding to the most probable interatomic separation in the liquid. These spacings are representative of highly correlated atomic arrangements, which are long lived because of the cooperative motions necessary for them to break up. This long lifetime is then reflected as a narrowing in energy width of $S(Q, \omega)$ for those Q's.

For CsC_{24} we have obtained similar results as for RbC_{24}, with the Cs structure factor exhibiting larger quasielastic linewidths at all temperatures (Fig. 2). The estimated diffusion constants, with the use of Eq. (1), are 5.7×10^{-5} cm^2/sec and 7.6×10^{-5} cm^2/sec for Rb and Cs, respectively, at 523 K.

While the features of the quasielastic spectra for alkali-metal intercalants, discussed so far, are qualitatively in agreement with what one would expect for a simple monatomic liquid, a closer inspection and comparison with 3D liquid Rb reveals some important differences:

(1) The quasielastic linewidth of liquid Rb (Ref. 8) shows a much larger energy broadening than those of 2D Rb layers at about the same temperature (Fig. 3).

(2) The dashed-dotted curve in Fig. 3 represents the ideal-gas limit for the quasielastic linewidth:

$$\Delta\omega_{\mathrm{IG}} = 2[2(\ln 2)K_B T/M]^{1/2} Q, \qquad (2)$$

where M is the mass of a single Rb atom. While the 3D liquid data approach the ideal-gas limit at large Q,[8] the data for Rb in graphite are far from this line, and preliminary triple-axis measurements at Q indicate that they will never approach this value. Therefore, the effective mass of the diffusing particles in the intercalant plane must be considerably larger than in free liquid Rb.

(3) We have observed here, as well as in an independent triple-axis study,[11] that collective phononlike excitations exist at Q values well beyond the maximum in the structure factor. This inelastic scattering, centered between 4 and 6 meV, is clearly separated from the quasielastic energy regime, indicating that diffusional and vibrational motions do not mix, even for small wavelength. 3D liquid Rb, in contrast, exhibits phononlike modes only at small wave vectors up to the first peak in the structure factor,[9] and for higher Q values one single quasielastic line is observed, implying that vibrational and diffusional excitations occur indistinguishably on the same time scale at these wave vectors.

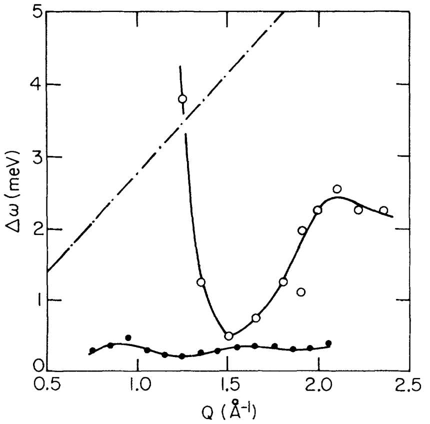

FIG. 3. Comparison of the Lorentzian linewidths for Rb diffusion in the free 3D liquid (open circles) and in between graphite planes (solid circles) at about the same temperature of 320 K. The 3-D liquid Rb data, taken from Ref. 8, show a minimum at $Q = 1.5$ Å^{-1}, and the Rb-intercalant data at about $Q = 1.22$ Å^{-1}, which is due to the differences in the structure factor. The dashed-dotted line indicates the energy width expected for an ideal gas of the same atomic mass [see Eq. (2)].

The present results clearly demonstrate that liquidlike diffusive motion of alkali-metal atoms exists within the intercalant planes in the high-temperature disordered state. The estimated diffusion constants are, however, roughly an order of magnitude smaller than those of 3D alkali-metal liquids. From a dynamical point of view, the disordered alkali-metal layers may be characterized as highly viscous and dense 2D fluids. These findings have an important impact on the understanding of the alkali-metal structures in graphite and may be of even wider relevance as a typical result for 2D monatomic liquids. This point will be further discussed later in this paper.

We note that the dynamical properties in question here arise from the migration of alkali-metal atoms in a completely filled intercalant layer, which is in thermodynamic equilibrium. This diffusion process, although not unrelated, must be distinguished from the diffusion occurring during intercalation and/or stage transformations. In the latter case considerably larger diffusion constants may be observed.[12]

One possible reason for the small diffusivity of alkali-metal atoms in graphite may be the alkali-metal–graphite interplanar interaction. The anisotropic liquid structure factor of Cs in CsC_{24}, noticeable in single-crystal x-ray photographs by Parry and Lester,[13] is pointing in this direction. On the other hand, recent Raman[14] and neutron spectroscopy[15] results revealed interlayer shear force constants between alkali-metal and graphite layers which are 5 to 10 times smaller than those between pristine graphite layers. Thus, the lateral motion of alkali-metal atoms experiences little shear resistance from the bonding graphite planes. We believe that the dominant effect on the low alkali-metal mobility originates from the dimensionality of the system. In a 2D densely packed structure, the migration of atoms becomes highly correlated because of the lack of vacancies and the motional freedom in the third dimension. These strong correlations, which decay slowly with respect to interlayer positions are, in turn, equivalent to an increased effective mass, as noted above. Therefore, in 2D intercalant planes, collective motion of alkali-metal atoms in the form of clusters is slow enough to support higher-frequency phononlike excitations of the intercalant atoms even at large wave vectors. Mention must be made of the fact that processes involving diffusion of dislocations, dislocation climbs, and grain boundary diffusion may be also present, but they possibly happen on time scales which are longer than the ones observed here. A final clarification on the different dynamical excitations present in 2D alkali-metal layers must come from a molecular dynamics calculation of the scattering law $S(Q,\omega)$, which is not available at the present time.

The coexistence of both collective diffusional and phononlike excitations to the extent reported here is unique and has not been observed for any 3D monatomic liquid. In this context one may speculate as to whether these coexisting dynamical modes are the fundamental excitations of the "floating solid" phase, proposed by Nelson and Halperin[16] for the melting of a 2D solid on a periodic substrate.

The present results manifest that AGIC's provide a unique test system for 2D liquid dynamics in theory as well as in experiment. In some sense, intercalation compounds may even be more suitable for these investigations than adsorbates on graphite,[17] since the problems connected with overlayers, pores, etc., evaporation, and hopping over other atoms are eliminated in the intercalalated alkali-metal layers, and pressure-dependent experiments are more readily performed. A more complete description, containing also results on stage-1 compounds, is in preparation.

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