

Wide Line Nuclear Magnetic Resonance of ^{19}F in Graphite–Antimony Pentafluoride: Evidence for Rapid Motion of Intercalated Species

By LAWRENCE B. EBERT,* ROBERT A. HUGGINS, and JOHN I. BRAUMAN

(Department of Chemistry and Department of Materials Science and Engineering, Stanford University, Stanford, California 94305)

Summary Antimony pentafluoride intercalated in graphite can display liquid-like behaviour at temperatures well below the freezing point of pure SbF_5 .

PREVIOUS research on order–disorder transformations in graphite intercalation compounds has not established the time scale of motion within the disordered phase.¹ We report here on the application of wide-line nuclear magnetic resonance to demonstrate the presence of high mobility of SbF_5 molecules intercalated in graphite. This motion can persist to temperatures at which the unintercalated SbF_5 phase is in the rigid lattice condition, although behaviour in this temperature range may arise from a supercooled state.

The compounds investigated are composed of graphite intercalated by varying amounts of SbF_5 . Synthesis by the method of Lalancette² led to materials of similar composition and thermal properties. X-Ray diffraction patterns, nevertheless, are not the same as reported, for we find definite evidence for the existence of stages (third stage compounds of c_0 ca. 15 Å and a fourth stage compound with c_0 ca. 18 Å) having a common graphite layer– SbF_5 –graphite

layer distance of ca. 8 Å. This distance occurs for a number of other graphite intercalation compounds,³ and its existence in this case reinforces the earlier suggestion⁴ of the importance of Brillouin zone effects in structural features of graphite compounds. Diffraction data are presented in the Table.

A plot of n.m.r. linewidth from derivative maximum to derivative minimum for SbF_5 , $\text{C}_{27}\text{SbF}_5$, and $\text{C}_{38}\text{SbF}_5$ against temperature is given in the Figure. Most striking is the observation that above -10°C , all three compounds possess fluorine resonances narrowed to the inhomogeneity limits of the magnet (0.2 G). Pulsed experiments determining T_1 at room temperature confirm this similarity in behaviour ($\text{C}_{38}\text{SbF}_5$, 71 ms; $\text{C}_{27}\text{SbF}_5$, 62 ms; SbF_5 , 43 ms). In the third stage compound $\text{C}_{27}\text{SbF}_5$, the narrow linewidth persists well below the temperature at which pure SbF_5 enters the rigid lattice regime.

Two arguments suggest that this line narrowing results from a translational motion of SbF_5 species. In wide line n.m.r. spectroscopy, a complete narrowing of the linewidth to the field inhomogeneity limit generally results from

TABLE

X-Ray diffraction patterns for three different graphite-SbF₅ intercalation compounds^a

C ₂₀ SbF ₅			C ₂₇ SbF ₅			C ₃₈ SbF ₅		
<i>d</i> /Å	(<i>hkl</i>)	<i>I</i>	<i>d</i> /Å	(<i>hkl</i>)	<i>I</i>	<i>d</i> /Å	(<i>hkl</i>)	<i>I</i>
15.2	001	w	14.5	001	vw			
7.37	002	w	7.25	002	vw			
4.90	003	w	4.87	003	w			
			4.48					
3.69	004	vs	3.67	004	vs	4.53	004	w
2.98	005	m	2.93	005	m	3.64	005	vs
2.12		w	2.12		vw	3.03	006	m
2.03	007	w	2.00	007	vw			
1.85	008	w	Not investigated			1.81	00-10	w
1.65	009	w				1.65	00-11	w

^a w = weak, m = medium, s = strong, v = very.

Compounds C₂₀SbF₅ and C₂₇SbF₅ are third stage with *c*₀ ca. 15 Å, and C₃₈SbF₅ is fourth stage with *c*₀ ca. 18 Å. After 4 months in a stoppered vial, C₂₇SbF₅ showed no change in either diffraction pattern or room-temperature n.m.r. linewidth. Lines in italics may represent graphite reflections.

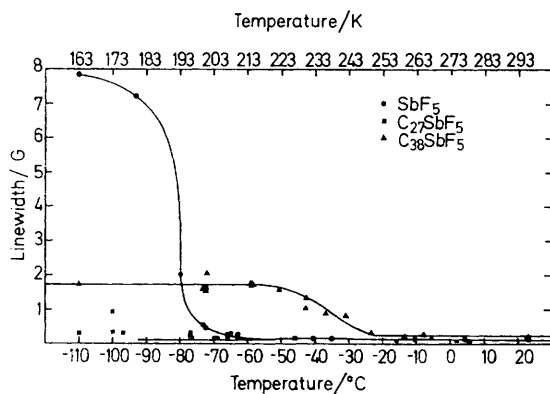


FIGURE. Magnetic resonance linewidth as a function of temperature for SbF₅, C₂₇SbF₅, and C₃₈SbF₅.

Data were taken at 4 MHz. No quantitative significance to the constructed lines is intended. In separate experiments, C₂₀SbF₅ showed a room-temperature linewidth of (0.3 ± 0.2) G and C₁₉SbF₅ showed a linewidth of (0.3 ± 0.2) G between -50 and 23 °C at both 4 and 16 MHz. Repeated cycling below -70 °C can produce hysteresis.

translational, rather than rotational motion. Furthermore, based on analogy to other graphite compounds,⁵ SbF₅ exists as chains of corner-shared octahedra not only in the free state but also in graphite. The constraint of inclusion in the layered lattice (ca. 5 Å available along the graphite *c* axis) would severely limit rotational freedom. The difference in behaviour of C₂₇SbF₅ and C₃₈SbF₅ is at present not understood, although it is felt that the intercalation stage, inserted molecule density for that stage, and possible co-inserted water molecules may affect the n.m.r. properties.

Both wide-line and pulsed n.m.r. experiments suggest that there is little interaction between the graphite and inserted SbF₅ molecules. Graphite is best viewed as a solvent, reducing the activity of the intercalated molecules without radically affecting their chemistry. From this and other work in our laboratory, we suggest that the presence of an extremely narrow line in the continuous wave n.m.r. spectrum may be correlated with a chemical activity of inserted molecule approaching that found in the free state.

This work was supported by the Office of Naval Research and the Advanced Research Projects Agency. One of us (L.B.E.) thanks the Fannie and John Hertz Foundation for fellowship support.

(Received, 4th July 1974; Com. 805.)

¹ A. R. Ubbelohde, *Proc. Roy. Soc.*, 1968, *A*, **304**, 297; 1972, *A*, **327**, 289; D. E. Nixon, G. S. Parry, and A. R. Ubbelohde, *ibid.*, 1966, *A*, **291**, 324; D. E. Nixon and G. S. Parry, *Nature*, 1967, **216**, 909.

² J. M. Lalancette and J. Lafontaine, *J.C.S. Chem. Comm.*, 1973, 815.

³ W. Rudorff and U. Hofmann, *Z. anorg. Chem.*, 1938, **238**, 1; W. Rudorff, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 223; Y. Takahashi, H. Yamagata, and T. Mukaibo, *Carbon*, 1973, **11**, 19.

⁴ L. B. Ebert, R. A. Huggins, and J. I. Brauman, *Carbon*, 1974, **12**, 199.

⁵ J. M. Cowley and J. A. Ibers, *Acta Cryst.*, 1956, **9**, 421.