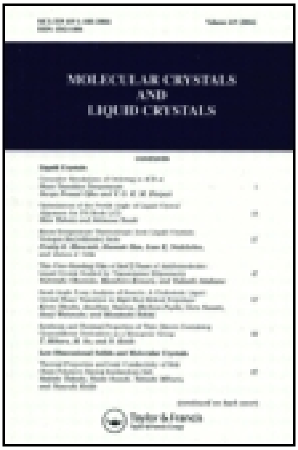

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Conduction electron spin resonance of ternary am-nh 3 -gics

Noboru Akuzawa [a] , Ken-Ichi Matsukita [a] , Hirokazu Yuasa [a] & Hiroaki Taono [a]
[a] Tokyo National College of Technology, 1220-2 Kunugida, Hachioji, Tokyo, 193-0997, Japan

Version of record first published: 18 Oct 2010

Mol. Cryst. Liq. Cryst., Vol. 387, pp. [397]/173–[402]/178

1058-725X/02 \$12.00 + .00
DOI: 10.1080/10587250290113745

CONDUCTION ELECTRON SPIN RESONANCE OF TERNARY AM-NH_3-GICs

Noboru Akuzawa, Ken-Ichi Matsukita,
Hirokazu Yuasa, and Hiroaki Taono
Tokyo National College of Technology,
1220-2 Kunugida, Hachioji, Tokyo 193-0997, Japan

Conduction electron spin resonance (CESR) of alkali metal-graphite intercalation compounds (AM-GICs) such as KC_8, KC_{24}, KC_{36}, RbC_8, RbC_{24} etc. and their ternary compounds with NH_3 was investigated. It was shown that ternary compound of RbC_8 with ammonia gave a clear ESR signal, in contrast to no signal for binary RbC_8 and that the line width of ESR spectra of $KC_8(NH_3)_x$ decreased monotonically with increasing ammonia content. These observations suggested that ammonia molecules reduce the spin-orbit interaction.

Keywords: intercalation; ternary GIC; nanospace; ESR

INTRODUCTION

The nanospace of alkali metal-graphite intercalation compounds such as CsC_{24} is able to accommodate a variety of molecules [1]. When ethylene is inserted in the nanospace of CsC_{24}, the resulting ternary compounds show a remarkable stability in air [2]. This is contrast to the ternary system, CsC_{24}-acetylene, which is not stable in air [3]. To understand the interaction between molecules inserted in the nanospace and the matrix, the electrical conductivity of CsC_{24} during sorption of various molecules was determined [4]. Acetylene (C_2H_2) caused remarkable decrease of the conductivity of CsC_{24}, while ethylene did not. To obtain further information about the interaction of molecules with AM-GICs matrix, the conduction electron spin resonance (CESR) of binary and ternary AM-GICs (AM = K, Rb, Cs) was investigated. As a first step, we focused on the ternary compounds of AM-GICs with ammonia, because ternarization takes place even for stage 1 MC_8 [5] and strong interaction with the matrix is expected in this system.

This work was partly supported by a Grant-in-Aid for "Research for the Future" Program "Nanocarbons" from the Japan Society for the Promotion of Science (JSPS).

EXPERIMENTAL

Materials

The host graphite material was Grafoil sheet (Ucar Carbon Company; GTA grade, thickness 0.4 mm). Typical sample dimensions were $l \times w \times d = 20 \times 4 \times 0.4\,mm^3$. It was degassed at ~1000°C in vacuo. Potassium, rubidium and cesium with purity of 99.95% were used after distillation.

Preparation of Binary and Ternary AM-GICs

AM-GICs were prepared by allowing alkali metal vapor to react with Grafoil sheet at 503 K, where the molar ratio of the supplied amounts of alkali metal and graphite (n_M/n_C) was adjusted to be the value corresponding to that of target AM-GICs. AM-GICs were then contacted with gaseous ammonia and the composition of the ternay compounds was determined based on the sorbed amount of ammonia.

ESR Measurement

AM-GICs were transferred to a glass tube for ESR measurement under vacuum. In the case of ternary AM-NH_3-GICs the sample was kept in the ESR glass tube under ammonia gas at equilibrium pressure. ESR spectra were measured using a conventional X-band spectrometer (JEOL, JES-TE100) with a rectangular TE_{102} microwave cavity. A static field H was applied parallel or perpendicular to the c-axis of the specimen.

RESULTS

All the ESR spectra of AM-GICs prepared from Grafoil and their ternary compounds with ammonia showed asymmetric Dysonian line shapes. The observed ESR signals of binary AM-GICs are shown in Figure 1, where the signals of Mn^{2+} (magnetic field marker) are seen in addition to the CESR signals of AM-GICs. No signal was observed for CsC_8 and CsC_{24} as reported by Muller and Kleiner [6].

The variation of ESR signals of KC_8 during ternarization with ammonia is shown in Figure 2. It can be seen that the line width decreased monotonically with increasing ammonia content.

Ammoniation of RbC_8 showed drastic change of ESR spectra as shown in Figure 3. The ESR signal of starting RbC_8 was not observed. However, $RbC_8(NH_3)_{0.18}$ showed a clear ESR signal.

In the cases of KC_{24} and RbC_{24}, the line width increased in the beginning of sorption, and then decreased with increasing ammonia content.

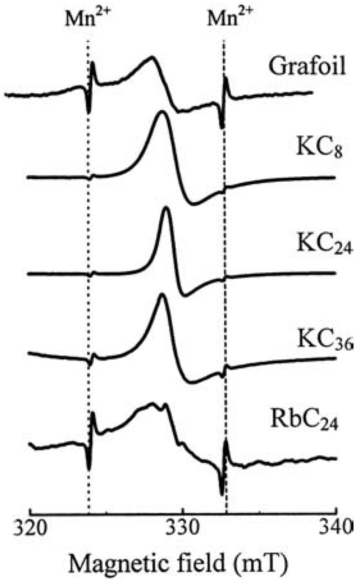

FIGURE 1 ESR spectra of Grafoil, KC_{24}, KC_8, KC_{36} and RbC_{24}.

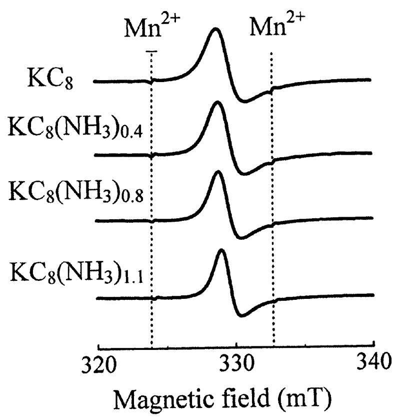

FIGURE 2 Variation of ESR spectrum of KC_8 during ammoniation.

DISCUSSION

ESR Parameters of Binary AM-GICs

The ESR parameters, A/B, g-value and line width (ΔH), were determined from the observed ESR signals. The g-value was calculated according to the

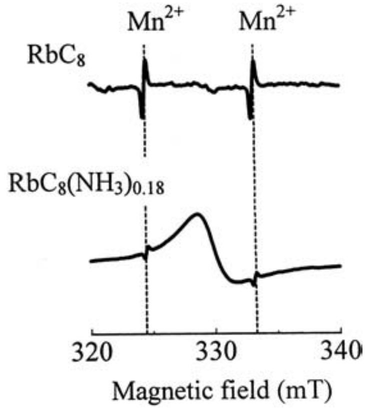

FIGURE 3 ESR spectra of RbC_8 and $RbC_8(NH_3)_{0.18}$.

Feher-Kip procedure [7] when the asymmetry parameter A/B was larger than 2.55. If A/B was smaller than 2.55, it was calculated according to the empirical rule which assumes that the resonance magnetic field is at the position where the signal intensity is 85% of the peak height [8]. The calculated values are given in Table 1, where literature values are also shown for comparison. The *g*-value of Grafoil had smaller anisotropy compared to natural graphite [9] and HOPG [10]. This can be attributed to poor stacking order of the crystallites of Grafoil. The g-values of AM-GICs determined in the present work were very close to the reported values [6]. The line width

TABLE 1 ESR Parameters of Grafoil and AM-GICs

	A/B		ΔH/gauss		$\Delta g^{*)} \times 10^4$	
Sample	$H_{//}$c	$H_{\perp}$c	$H_{//}$c	$H_{\perp}$c	$H_{//}$c	$H_{\perp}$c
Grafoil	2.38	2.43	23.4	19.8	+290	+53
Natural graphite [9]			4.6	3.0	+472	+9
HOPG [10]					+435	+9
KC_8	2.44	2.43	17.1	18.1	+4	+10
KC_8 [6]			11.4	12.6	0	+14
KC_{24}	2.57	2.61	11.1	10.1	−1	+6
KC_{24} [6]			3.9		+1	+9
RbC_{24}	2.76	2.46	37.2	36.4	+28	+11
RbC_{24} [6]			28.7		+30	+40

$^{*)}\Delta g = g(\text{observed}) - 2.0023$.

(ΔH), however, was several times larger than the reported values. This may be also due to the poor stacking order of the crystallites of Grafoil noted above. Values of g factor and ΔH were independent of temperature between 100 and 300 K, in agreement with literature [11].

ESR Parameters of AM-NH_3-Ternary GICs

No signal was observed for $CsC_8(NH_3)_X$ and $CsC_{24}(NH_3)_x$, similarly to the binary CsC_8 and CsC_{24}. This can be attributed to the spin orbit interaction. Values of Δg and ΔH of $KC_8(NH_3)_x$, $RbC_8(NH_3)_x$, $KC_{24}(NH_3)_x$ and $RbC_{24}(NH_3)_x$ determined at room temperature are given in Table 2. The values of Δg were independent of ammonia content. It was also confirmed that the value of Δg was constant between 100 and 300 K for $RbC_8(NH_3)_{0.83}$ $KC_{24}(NH_3)_{3.4}$. The line width (ΔH) of $KC_8(NH_3)_x$ was plotted against ammonia content (n_{NH_3}/n_{KC_8}) in Fig. 4. Value of ΔH decreased monotonically with increasing n_{NH_3}/n_{KC_8}. Taking into account additionally the fact that a clear ESR signal was observed for

TABLE 2 ESR Parameters of $MC_x(NH_3)_y$

	A/B		ΔH/gauss		$\Delta g \times 10^4$	
Sample	$H_{//}$c	$H_{\perp}$c	$H_{//}$c	$H_{\perp}$c	$H_{//}$c	$H_{\perp}$c
$KC_8(NH_3)_{1.1}$	2.52	2.60	10.1	10.2	+11	+10
$KC_{24}(NH_3)_{2.4}$	2.06	2.46	9.2	9.7	+11	+7
$RbC_8(NH_3)_{0.9}$	–	2.61	–	35.7	–	+22
$RbC_{24}(NH_3)_{2.1}$	2.63	2.84	29.4	29.8	+10	+18

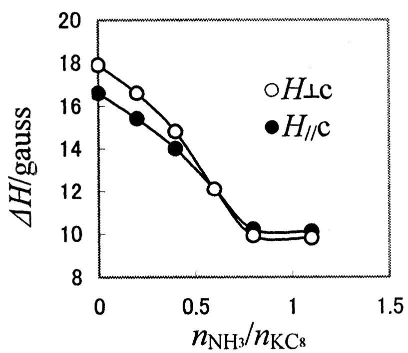

FIGURE 4 Value of ΔH plotted as a function of n_{NH_3}/n_{KC_8} for $KC_8(NH_3)_x$.

$RbC_8(NH_3)_{0.18}$, it is considered that ammonia molecules inserted in the nanospace of MC_8 reduce the spin-orbit interaction.

CONCLUSIONS

Conduction electron spin resonance (CESR) of alkali metal-graphite intercalation compounds (AM-GICs) such as KC_8, KC_{24}, KC_{36}, RbC_8, RbC_{24} etc. and their ternary compounds with NH_3 was investigated. It was confirmed that ternary compound of RbC_8 with ammonia gave a clear ESR signal, in contrast to binary RbC_8. It was also shown that the line width of ESR spectra of $KC_8(NH_3)_x$ decreased monotonically with increasing ammonia content. These observations suggested that ammonia molecules reduce the spin-orbit interaction. For the cases of the ammoniation of KC_{24} and RbC_{24}, the line width increased in the beginning of sorption, and then decreased with increasing ammonia content.

REFERENCES

[1] Watanabe, K., Kondow, T., Soma, M., Onishi, M., & Tamaru, K. (1973). *Proc. Roy. Soc. Lond.*, *A333*, 51.
[2] Takahashi, Y., Oi, K., Terai, T., & Akuzawa, N. (1991). *Carbon*, *29*, 283.
[3] Takahashi, Y., Oi, K., Yoneoka, T., Terai, T., & Akuzawa, N. (1995). *Proc. 20th Bien. Conf. Carbon*, 652.
[4] Akuzawa, N., Yamamoto, K., & Takahashi, Y. (2001). *Carbon*, *39*, 300.
[5] Akuzawa, N., Kawahara, S., Sakuno, H., Amemiya, T., & Takahashi, Y. (1988). *Carbon*, *26*, 104.
[6] Muller, K. A. & Kleiner, R. (1962). *Phys. Lett.*, *1*, 98.
[7] Dresselhaus, M. S. & Dresselhaus, G. (1981). *Adv. Phys.*, *30*, 139.
[8] Delhaes, P., Amiell, J., Ohhashi, K., Mareche, J. F., Guerard, D., & Herold, A. (1983). *Synth. Met.*, *8*, 269.
[9] Akuzawa, N., Watanabe, M., Tajima, T., Soneda, Y., Matsumoto, R., & Takahashi, Y. *Synth. Met.*, (in press).
[10] Lauginie, P., Estrade, H., Conard, J., Guerard, D., Lagrange, P., & Makrini, M. El. (1980). *Physica*, *99B*, 514.
[11] Delhaes, P., Amiell, J., Ohhashi, K., Mareche, J. F., Guerard, D., & Herold, A. (1983). *Synth. Met.*, *8*, 269.