

Assignment of ^{39}K NMR signals for potassium–graphite intercalation compound KC_8

Hideka Ando ^{1*}, Shinobu Ohki², Yuuki Mogami², Kazuma Gotoh³, Kenjiro Hashi⁴

¹International Center for Young Scientists, National Institute for Materials Science, 3-13 Sakura, Tsukuba, Ibaraki 305-0003, Japan

²Advanced Engineering and Services Division, National Institute for Materials Science, 3-13 Sakura, Tsukuba, Ibaraki 305-0003, Japan

³Center for Nano Materials and Technology, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

⁴Center for Basic Research on Materials, National Institute for Materials Science, 3-13 Sakura, Tsukuba, Ibaraki 305-0003, Japan

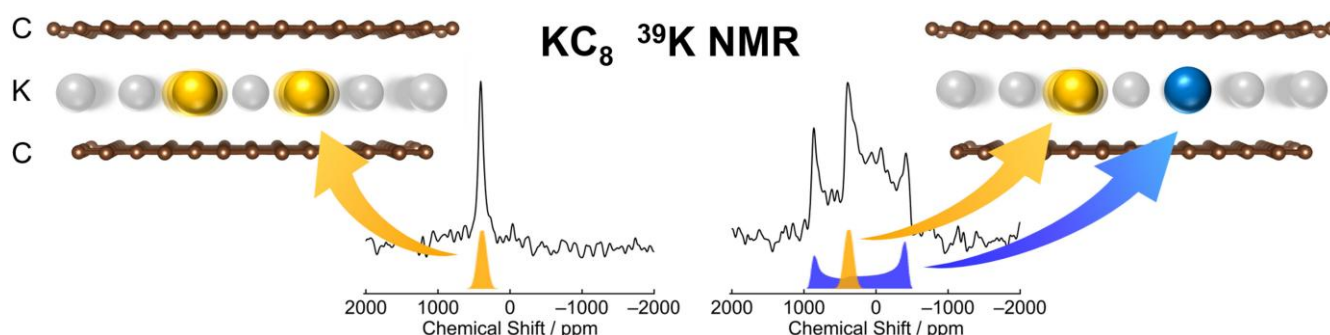
*Corresponding author: International Center for Young Scientists, National Institute for Materials Science, 3-13 Sakura, Tsukuba, Ibaraki 305-0003, Japan.
Email: ANDO.Hideka@nims.go.jp

Abstract

Potassium–graphite intercalation compounds (K–GICs) have potential applications in potassium–ion batteries. Although previous research has reported solid-state nuclear magnetic resonance (NMR) measurements on K–GICs, the assignment of their ^{39}K NMR spectra remains unclear. In this study, we provide new insights into the ^{39}K NMR spectral assignment for K–GICs and reveal that the state of the intercalated potassium ions varies even for compounds with the same composition.

Keywords graphite intercalation compound, potassium, solid-state nuclear magnetic resonance

Graphical Abstract



Graphite intercalation compounds (GICs) are a family of materials formed by intercalating guest atoms or molecules between the graphene layers of a host graphite.¹ Graphite intercalation compounds possess a variety of attractive chemical and physical properties such as high electrical conductivity,^{2,3} superconductivity,^{4–6} and hydrogen storage capacity,^{7,8} making them important candidates for use in a wide range of fields. Graphite intercalation compounds form a layered arrangement described as “stage n ,” where the index “ n ” refers to the number of graphene layers between adjacent intercalated layers. For example, stage 1 compounds include alternate graphene and intercalated layers. Among the various guest species suitable for GIC formation, potassium is widely studied as an intercalant.^{1,9} Stage 1 potassium–GICs

(K–GICs) have the composition KC_8 , in which the potassium ions are periodically arranged between the graphene layers to form a $p(2 \times 2)R0^\circ$ superlattice. Furthermore, the overall crystal structure exhibits an $\text{A}\alpha\text{A}\beta\gamma\text{A}\delta$ stacking sequence along the c -axis, where A denotes the position of the host (graphene) layers, while α , β , γ , and δ denote the registry sites occupied by the intercalated metal species.^{10,11} In recent years, K–GICs have attracted much attention because of their potential application in next-generation energy storage devices, especially potassium–ion batteries (KIBs).^{12–14} Potassium–ion batteries comprise low-cost and nontoxic elements, which have abundant reserves in the Earth’s crust.¹⁵ In addition, KIBs are expected to show high operating voltages and deliver rapid charge–discharge performance.^{16,17} To fully utilize

Received: 27 July 2026. Revised: 25 August 2026. Accepted: 27 August 2026. Corrected and typeset: 22 September 2026.

© The Author(s) 2026. Published by Oxford University Press on behalf of the Chemical Society of Japan.

This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<https://creativecommons.org/licenses/by/4.0/>), which permits unrestricted reuse, distribution, and reproduction in any medium, provided the original work is properly cited.

these advantages for KIBs, it is crucial to further probe the storage position and dynamics of potassium in graphite.

Solid-state nuclear magnetic resonance (NMR) is a potentially powerful tool for investigating the local environment and state of potassium in K-GICs. However, NMR measurements of potassium nuclei are extremely challenging because of their low sensitivity resulting from the small gyromagnetic ratio.¹⁸ In addition, the high reactivity and electrical conductivity of potassium-stored carbon materials further complicate NMR measurements. We successfully observed the ^{39}K NMR signals of K-GICs for the first time in 2024.¹⁹ Nevertheless, the spectra exhibited complex features with multiple peaks, even though Raman spectroscopy indicated the formation of the simple GIC structure with a single coordination environment of potassium ions. As a result, the assignment of these signals remained unsuccessful. In this study, we successfully accomplished this signal assignment by performing ^{39}K NMR measurements on both commercial and synthesized KC_8 samples under various conditions, thus obtaining new insights into the state of potassium in graphite.

Commercial KC_8 , manufactured by Strem Chemicals, Inc., was purchased from FUJIFILM Wako Pure Chemical Corp. The synthesized KC_8 was prepared as follows. SP-1 graphite powder (Bay Carbon, Inc.) and potassium metal (Sigma-Aldrich Co. LLC) were sealed in a glass tube under vacuum at the stoichiometric ratio of KC_8 . The sealed mixture was heated at 370 °C for 48 h. For NMR measurements, approximately 40 to 50 mg of these samples were mixed with polyvinylidene difluoride (PVDF) and sealed in a glass tube, as described in our previous report.¹⁹ ^{39}K NMR measurements were performed using an NMR spectrometer equipped with an 18.79 T magnet (JNM-ECZ800R; JEOL), corresponding to a resonance frequency of 37.3 MHz for ^{39}K . For comparison, measurements were also carried out using a spectrometer equipped with an 11.75 T magnet (JNM-ECZ500R; JEOL), at a resonance frequency of 23.3 MHz. All measurements were performed under static conditions using an Oldfield echo²⁰ and single pulse sequences. For the Oldfield echo sequence, each pulse width was set to 8 μs for the measurements at 18.79 T and 10 or 12 μs for the measurements at 11.75 T. The interval between two pulses was set to 150 μs , and the recycle delay was 1 s. The spectra at 18.79 T were obtained by accumulating approximately 86,000 transients in 1 day, whereas the spectra at 11.75 T were acquired over more than 1 week. For the single pulse sequence, the pulse length was 5 μs , with a recycle delay of 1 s. KBr aqueous solution was used as a reference at 0 ppm. The 90° pulse lengths determined using the reference were 12 μs at 18.79 T and 17 μs at 11.75 T.

The electric field gradient (EFG) of KC_8 was calculated by the density functional theory (DFT) using the gauge-including projector augmented wave approach.²¹ Density functional theory calculations were performed using Quantum ESPRESSO 7.1²² with the PS-library as the pseudopotential.²³ The Perdew–Burke–Ernzerhof exchange–correlation function was adopted. The input file for the calculation was generated with help of the cif2cell program.²⁴ The Monkhorst–Pack k -point mesh was set to $4 \times 4 \times 4$. The cutoff energy of the system was set to 80 Ry. The crystal structure of KC_8 was obtained from the Materials Project database (material ID: mp-28930).²⁵ The theoretical powder NMR spectrum for the quadrupolar nucleus was calculated using a program written by the author, based on the second-order perturbation theory for quadrupole interaction.²⁶

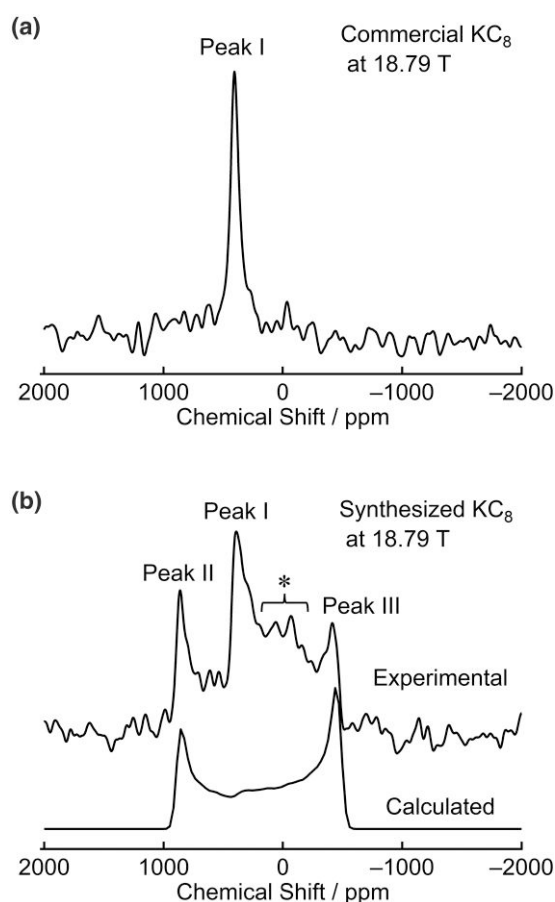


Figure 1 a) ^{39}K NMR spectrum of commercial KC_8 (Oldfield echo sequence, 18.79 T). b) Top: ^{39}K NMR spectrum of synthesized KC_8 (Oldfield echo sequence, 18.79 T); bottom: calculated spectrum with $C_Q = 3.8$ MHz and $\eta = 0$. The peaks are labeled as Peak I, Peak II, and Peak III, respectively, for identification. The asterisk (*) denotes a broad signal, attributed to decomposition and components with structural changes.

The ^{39}K NMR spectra of the commercial and synthesized KC_8 samples revealed distinctive differences in their spectral features, as shown in Fig. 1. In the spectrum of the commercial KC_8 sample measured using the Oldfield echo sequence, a single sharp peak was observed around 407 ppm (Peak I in Fig. 1a), consistent with our previous study using the single pulse sequence.¹⁹ This observation suggests that all potassium ions in the commercial KC_8 sample exist in the same local environment on the time-scale of the 1D NMR measurements. In contrast, the spectrum of the synthesized KC_8 sample exhibited a much more complex line shape (top part of Fig. 1b). The ^{39}K NMR spectrum measured using the Oldfield echo sequence exhibited a broad and asymmetric signal with pronounced tips around 862, 393, and -415 ppm, which are labeled as Peak II, Peak I, and Peak III, respectively, in Fig. 1b for identification. Additionally, a broad signal around 0 ppm was also observed (*) in Fig. 1b, which is likely attributed to decomposition and components with structural changes. When using the single pulse sequence, three clear peaks were detected at the same position as the tips observed with the echo sequence (Supplementary Fig. S1). This observation is similar to our previous findings for synthesized stage 2 and stage 3 K-GIC samples.¹⁹ However, the peak positions are different from those observed in the spectrum of KC_8 . Notably, the large

positive shift for the KC_8 sample is attributed to the Knight shift, as also reported for stage 1 lithium–GICs.²⁷

The broad and asymmetric line shape composed of Peak II and Peak III in the spectrum of the synthesized KC_8 sample resembles the powder pattern of the central transition for the quadrupolar nuclei, which is affected by second-order quadrupolar interactions. To investigate this possibility, the EFG at the potassium site in the commonly proposed KC_8 structure was estimated using DFT calculations. The resulting quadrupole coupling constant (C_Q) and the asymmetric parameter (η) were 3.97 MHz and 0.02, respectively. To confirm the accuracy of these values, we calculated the quadrupolar powder pattern. By systematically increasing C_Q in steps of 0.1 MHz and η in steps of 0.1, we achieved the best agreement with the experimental spectrum at $C_Q = 3.8$ MHz and $\eta = 0$, as shown in the bottom part of Fig. 1b. To reflect isotropic shifts, including the Knight shift, a shift of 420 ppm to the higher frequency side was applied to the calculated spectrum. This agreement between the experimental and theoretical values confirmed that the broad and asymmetric line arises from the potassium ions located at the proposed sites in the KC_8 structure.

To further confirm that the observed signal originates from a quadrupolar powder pattern, we performed NMR measurements at a different magnetic field strength (11.75 T). If the line shape is a quadrupolar powder pattern, the linewidth should increase at lower magnetic fields. As expected, the spectrum measured at 11.75 T exhibited broadening of the main signals, as shown in Fig. 2 and Supplementary Fig. S2. Given the excessive broadening, spectra were recorded with the observation center set at 0 and 1,500 ppm to cover the entire spectral width. Upon combining these spectra, horns corresponding to Peak II and Peak III were identified around 1,611 and $-1,693$ ppm at the edges of the signal, confirming that these components are dependent of the magnetic field strength. A theoretical NMR spectrum calculated using $C_Q = 3.8$ MHz and $\eta = 0$ at 11.75 T (^{39}K resonance frequency: 23.3 MHz) exhibited two horns that closely matched the positions of the experimentally observed horns, as shown in the bottom part of Fig. 2. These results serve as evidence for the two horns (Peak II and Peak III) originating from a second-order

quadrupolar powder pattern. The position of the sharp peak around 400 ppm (Peak I), observed at a high magnetic field of 18.79 T, remained unchanged with field strength.

The aforementioned findings indicated the coexistence of at least two types of potassium ions in the synthesized KC_8 sample. The broad and asymmetric signal with pronounced tips at 862 (Peak II) and -415 ppm (Peak III) was attributed to the quadrupolar powder pattern, indicating that some potassium ions experience a strong EFG. Our calculation results strongly supported the assignment of this signal to intercalated potassium ions in the commonly proposed KC_8 structure. On the other hand, the sharp peak observed at around 400 ppm (Peak I) was attributed to the potassium ions that are probably unaffected by the EFG. The large positive shift due to the Knight shift suggests that these potassium ions are also located at the interlayer sites. The signal observed for the commercial KC_8 sample appeared to correspond to Peak I. Assuming a linear relationship between the atomic charge and the Knight shift, as reported for lithium,²⁸ and based on the shift of 2,640 ppm for potassium metal¹⁹ (charge 0) and 0 ppm for potassium ion (charge +1), the charge on the potassium atoms in stage 1 K–GICs was estimated to be +0.85. This estimated value shows good agreement with previously reported results.²⁹ The origin of these two distinct potassium ions is currently under investigation. Nevertheless, these two species are speculated to correspond to potassium ions with slow and fast dynamics. These ionic behaviors are likely linked to the crystallinity of the host graphite, such as the crystallite size and the amount of defect.

In conclusion, this study successfully assigns the previously unclarified ^{39}K NMR spectra of K–GICs. The complicated NMR spectra observed in the synthesized KC_8 samples can be attributed to at least two types of intercalated potassium ions: those experiencing an EFG and those that behave as if they do not. Notably, the significant difference between the NMR spectra of the commercial and synthesized KC_8 samples reveals that the state of the intercalated potassium ions can differ even among compounds with the same composition. Although further investigation is required to clarify the origin of these potassium ions, a possible explanation is the difference in the dynamics of the ions. Our findings would make a significant contribution to the understanding of the state of potassium in graphite. These insights are expected to play an important role in the development of advanced graphene-based materials.

Acknowledgments

This work was supported by “Advanced Research Infrastructure for Materials and Nanotechnology in Japan (ARIM)” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), proposal number JPMXP1225NM5323. Additionally, we acknowledge the ICYS research fellowship from NIMS. We would like to thank Editage (www.editage.jp) for English language editing.

Supplementary material

Supplementary material is available at Chemistry Letters online.

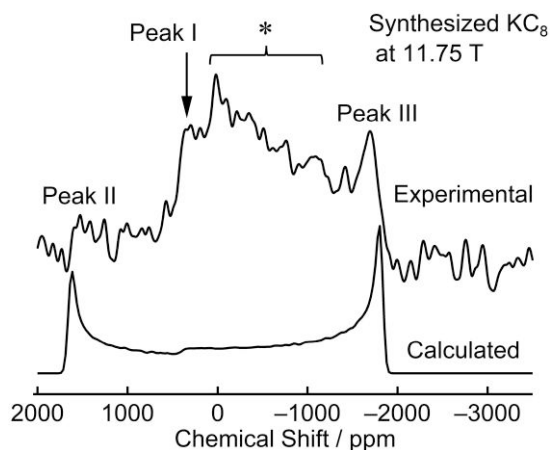


Figure 2 Top: ^{39}K NMR spectrum of synthesized KC_8 measured with the observation center set to 0 ppm (Oldfield echo sequence, 11.75 T); bottom: calculated spectrum with $C_Q = 3.8$ MHz and $\eta = 0$. The peaks are labeled as Peak I, Peak II, and Peak III, respectively, for identification. The asterisk (*) denotes a broad signal, attributed to decomposition and components with structural changes.

Funding

This work was supported by Japan Society for the Promotion of Science (JSPS) Grants-in-Aid for Scientific Research (KAKENHI), grant number JP25K23614.

Conflicts of interest

None declared.

References

1. M. S. Dresselhaus, G. Dresselhaus, *Adv. Phys.* **2002**, *51*, 1. <https://doi.org/10.1080/00018730110113644>.
2. M. Inagaki, *J. Mater. Res.* **1989**, *4*, 1560. <https://doi.org/10.1557/JMR.1989.1560>.
3. R. Matsumoto, Y. Okabe, *Synth. Met.* **2016**, *222*, 351. <https://doi.org/10.1016/j.synthmet.2016.11.020>.
4. N. B. Hannay, T. H. Geballe, B. T. Matthias, K. Andres, P. Schmidt, D. MacNair, *Phys. Rev. Lett.* **1965**, *14*, 225. <https://doi.org/10.1103/PhysRevLett.14.225>
5. Y. Koike, H. Suematsu, K. Higuchi, S. Tanuma, *Solid State Commun.* **1978**, *27*, 623. [https://doi.org/10.1016/0038-1098\(78\)90457-X](https://doi.org/10.1016/0038-1098(78)90457-X).
6. R. Matsumoto, M. Nakajima, Y. Takano, Y. Mizuguchi, N. Akuzawa, *Solid State Commun.* **2012**, *152*, 767. <https://doi.org/10.1016/j.ssc.2012.01.049>.
7. A. Lovell, F. Fernandez-Alonso, N. T. Skipper, K. Refson, S. M. Bennington, S. F. Parker, *Phys. Rev. Lett.* **2008**, *101*, 126101. <https://doi.org/10.1103/PhysRevLett.101.126101>
8. G. Srinivas, A. Lovell, C. A. Howard, N. T. Skipper, M. Ellerby, S. M. Bennington, *Synth. Met.* **2010**, *160*, 1631. <https://doi.org/10.1016/j.synthmet.2010.05.032>.
9. K. Fredenhagen, G. Cadenbach, *Z. Anorg. Allg. Chem.* **1926**, *158*, 249. <https://doi.org/10.1002/zaac.19261580122>.
10. W. Rüdorff, E. Schulze, *Z. Anorg. Allg. Chem.* **1954**, *277*, 156. <https://doi.org/10.1002/zaac.19542770307>.
11. D. E. Nixon, G. S. Parry, *J. Phys. D. Appl. Phys.* **1968**, *1*, 303. <https://doi.org/10.1088/0022-3727/1/3/303>.
12. Z. Jian, W. Luo, X. Ji, *J. Am. Chem. Soc.* **2015**, *137*, 11566. <https://doi.org/10.1021/jacs.5b06809>.
13. W. Luo, J. Wan, B. Ozdemir, W. Bao, Y. Chen, J. Dai, H. Lin, Y. Xu, F. Gu, V. Barone, L. Hu, *Nano Lett.* **2015**, *15*, 7671. <https://doi.org/10.1021/acs.nanolett.5b03667>.
14. J. Xu, Y. Dou, Z. Wei, J. Ma, Y. Deng, Y. Li, H. Liu, S. Dou, *Adv. Sci.* **2017**, *4*, 1700146. <https://doi.org/10.1002/adv.201700146>.
15. R. L. Rudnick, S. Gao, *Treatise on Geochemistry*, Elsevier, Amsterdam, Netherlands, **2003**, p. 1–64. <https://doi.org/10.1016/B0-08-043751-6/03016-4>.
16. S. Komaba, T. Hasegawa, M. Dahbi, K. Kubota, *Electrochem. Commun.* **2015**, *60*, 172. <https://doi.org/10.1016/j.elecom.2015.09.002>.
17. T. Hosaka, K. Kubota, A. S. Hameed, S. Komaba, *Chem. Rev.* **2020**, *120*, 6358. <https://doi.org/10.1021/acs.chemrev.9b00463>.
18. M. E. Smith, *Magn. Reson. Chem.* **2021**, *59*, 864. <https://doi.org/10.1002/mrc.5116>.
19. H. Ando, K. Hashi, S. Ohki, R. Matsumoto, K. Gotoh, *Chem. Lett.* **2024**, *53*, upae195. <https://doi.org/10.1093/chemle/upae195>.
20. A. C. Kunwar, G. L. Turner, E. Oldfield, *J. Magn. Reson.* **1986**, *69*, 124. [https://doi.org/10.1016/0022-2364\(86\)90224-6](https://doi.org/10.1016/0022-2364(86)90224-6).
21. C. J. Pickard, F. Mauri, *Phys. Rev. B* **2001**, *63*, 245101. <https://doi.org/10.1103/PhysRevB.63.245101>
22. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, R. M. Wentzcovitch, *J. Phys. Condens. Matter* **2009**, *21*, 395502. <https://doi.org/10.1088/0953-8984/21/39/395502>.
23. A. Dal Corso, *Comput. Mater. Sci.* **2014**, *95*, 337. <https://doi.org/10.1016/j.commatsci.2014.07.043>.
24. T. Björkman, *Comput. Phys. Commun.* **2011**, *182*, 1183. <https://doi.org/10.1016/j.cpc.2011.01.013>.
25. A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K. A. Persson, *APL Mater.* **2013**, *1*, 011002. <https://doi.org/10.1063/1.4812323>.
26. J. T. Cheng, J. C. Edwards, P. D. Ellis, *J. Phys. Chem.* **1990**, *94*, 553. <https://doi.org/10.1021/j100365a014>.
27. K. Zaghbi, K. Tatsumi, Y. Sawada, S. Higuchi, H. Abe, T. Ohsaki, *J. Electrochem. Soc.* **1999**, *146*, 2784. <https://doi.org/10.1149/1.1392009>.
28. D. C. Maxwell, C. A. O'Keefe, C. Xu, C. P. Grey, *Phys. Rev. Mater.* **2023**, *7*, 065402. <https://doi.org/10.1103/PhysRevMaterials.7.065402>
29. G. Louprias, S. Rabii, J. Tarbès, S. Nozières, R. C. Tatar, *Phys. Rev. B* **1990**, *41*, 5519. <https://doi.org/10.1103/PhysRevB.41.5519>