

Phase transitions in $\text{Na}_2\text{AC}_{60}$ ($A = \text{Cs, Rb, and K}$) fullerenes

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The ternary system fullerenes $\text{Na}_2\text{AC}_{60}$ ($A = \text{Cs, Rb, and K}$) are studied by differential scanning calorimetry in the temperature range of 100 to 450 K. All show reproducible phase transitions at the transition temperatures of 299 K ($\Delta H = 2.5 \pm 0.5$ J/g) for $\text{Na}_2\text{CsC}_{60}$, 313 K ($\Delta H = 2.7 \pm 0.5$ J/g) for $\text{Na}_2\text{RbC}_{60}$, and 305 K ($\Delta H = 3.1 \pm 0.5$ J/g) for $\text{Na}_2\text{KC}_{60}$. Orientational ordering of the fullerene unit is responsible for the observed phase transitions ($T_{\text{sc-fcc}}$) from a high-temperature face-centered-cubic (fcc) to a low-temperature simple-cubic (sc) phase. The observed $T_{\text{sc-fcc}}$ and enthalpy can be compared to those for pristine C_{60} which has $T_{\text{sc-fcc}} = 256.5$ K ($\Delta H = 8 \pm 0.5$ J/g). The observed behavior is discussed in terms of the balance between the $\text{C}_{60}^{3-} - \text{C}_{60}^{3-}$ intermolecular interaction and the $\text{C}_{60}^{3-} - A^+$ Coulombic interaction as a function of lattice parameter.

A lot of attention has been paid to alkali C_{60} fullerenes because they show both conductivity¹ and superconductivity.²⁻⁵ Superconductivity is observed generally in the face centered cubic (fcc) crystal phases in $A_3\text{C}_{60}$ compositions (where A denotes the alkali metal). The relationship between superconducting transition temperature (T_c) and crystal structure is an important issue for understanding the mechanism of the superconductivity. So far the T_c has been considered to be most likely controlled by the density of states at the Fermi level within the framework of BCS theory, that is the T_c increases with the lattice expansion because of the band narrowing.^{6,7} However, exceptions have now been found for Na- and Li-containing fullerenes.⁸⁻¹¹ Studies of T_c versus lattice parameters (a_0) in ternary $\text{Na}_2\text{AC}_{60}$ and $\text{Li}_2\text{AC}_{60}$ revealed that such simple relationship is no longer valid^{10,11} since some of these fullerenes show T_c 's far below expectation.⁸ For instance, $\text{Na}_2\text{RbC}_{60}$ shows superconductivity at $3.5(\pm 1)$ K which is far less than the expected 10 K from the high-pressure experiments on K_3C_{60} and Rb_3C_{60} .^{8,10} Furthermore, $\text{Li}_2\text{AC}_{60}$ fullerenes do not superconduct down to 50 mK.¹¹ The reason for these features cannot be explained in terms of the disproportionation type phase transition reported for Na_3C_{60} , which separates at low temperatures into two nonsuperconducting fcc phases, Na_2C_{60} and Na_6C_{60} .⁹

Recently $\text{Na}_2\text{RbC}_{60}$ was shown to have a simple cubic (sc) ($Pa\bar{3}$) structure at low temperatures by high resolution x-ray experiments.¹² Furthermore, neutron diffraction revealed that $\text{Na}_2\text{CsC}_{60}$ is also sc at low temperatures and shows the order-disorder phase transition to an fcc phase upon heating.¹³ These findings of the crystal structure for the Na-containing C_{60} fullerenes are very important for understanding superconductivity in $A_3\text{C}_{60}$ compounds and further study of these phase transitions is warranted.

In the present study, we have prepared high quality single-phase $\text{Na}_2\text{AC}_{60}$ (where $A = \text{K, Rb, and Cs}$) and searched the C_{60} order-disorder type sc-fcc phase transition by differential scanning calorimetry (DSC). We

show that this phase transition occurs in all of the $\text{Na}_2\text{AC}_{60}$ fullerenes with higher transition temperatures ($T_{\text{sc-fcc}}$) and lower enthalpy change than those encountered in pristine C_{60} .

$\text{Na}_2\text{AC}_{60}$ ($A = \text{Cs, Rb, and K}$) compounds were prepared using the method reported before.^{8,10} Careful handling of the stoichiometry and relatively long intermittent shaking during the thermal diffusion stage gave much better quality $\text{Na}_2\text{KC}_{60}$ than previously. 10 to 30 mg of the $\text{Na}_2\text{AC}_{60}$ samples were hermetically sealed in 6-ml Al pans and DSC measurements were carried out in the temperature range of 100 to 450 K at a rate of 10 K/min using a Mettler DSC 3000 instrument with a low-temperature attachment in the high sensitivity mode. Hysteresis of roughly 3 K was observed for all $\text{Na}_2\text{AC}_{60}$ samples between heating and cooling processes with almost the same enthalpy. The quality of the samples was followed before and after the DSC measurements by x-ray diffraction in order to confirm that no degradation occurred during the experiments.

X-ray diffractions of $\text{Na}_2\text{AC}_{60}$ ($A = \text{Cs, Rb, and K}$) were measured at room temperature as shown in Fig. 1 in order to confirm the sample quality before DSC experiments. The diffraction from the $\text{Na}_2\text{KC}_{60}$ shows a nearly single-crystal phase at room temperature within the resolution of our experiments. Since the DSC data discussed later show that the phase transition is very close to room temperature, the observed x-ray diffractions apparently contain both sc and fcc phases. However it should be noted that these samples are far better than those of earlier studies.^{8,10}

The DSC measured on $\text{Na}_2\text{AC}_{60}$ ($A = \text{K, Rb, and Cs}$) exhibited endothermic peaks at 299 ± 3 K ($\Delta H = 2.5 \pm 1.0$ J/g) for $\text{Na}_2\text{CsC}_{60}$, 313 ± 3 K ($\Delta H = 2.7 \pm 1.0$ J/g) for $\text{Na}_2\text{RbC}_{60}$ and 305 ± 3 K ($\Delta H = 3.1 \pm 1.0$ J/g) for $\text{Na}_2\text{KC}_{60}$ as shown in Fig. 2. No sign of unreacted C_{60} showing the known sc to fcc transition at around 260 K ($\Delta H = 8 \pm 0.3$ J/g) (Refs. 14-27) was detected. Under the same experimental conditions, no peaks were observed for K_3C_{60} and Rb_3C_{60} in the temperature range of 100 to

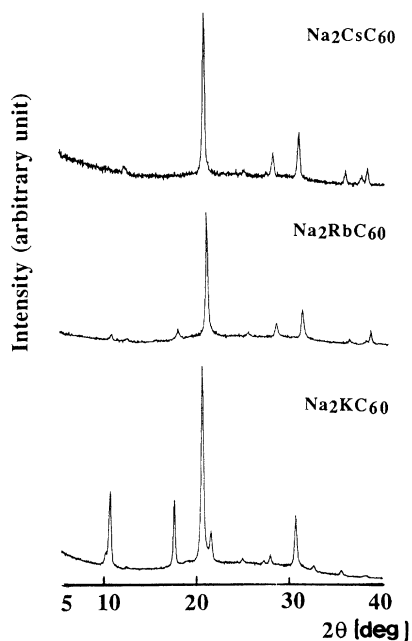


FIG. 1. X-ray diffractions of $\text{Na}_2\text{AC}_{60}$ ($A = \text{Cs, Rb, and K}$). The asterisks are due to the scattering from Al sample holder. The diffraction of $\text{Na}_2\text{KC}_{60}$ can roughly be interpreted as a sc and/or fcc lattice as described in the text.

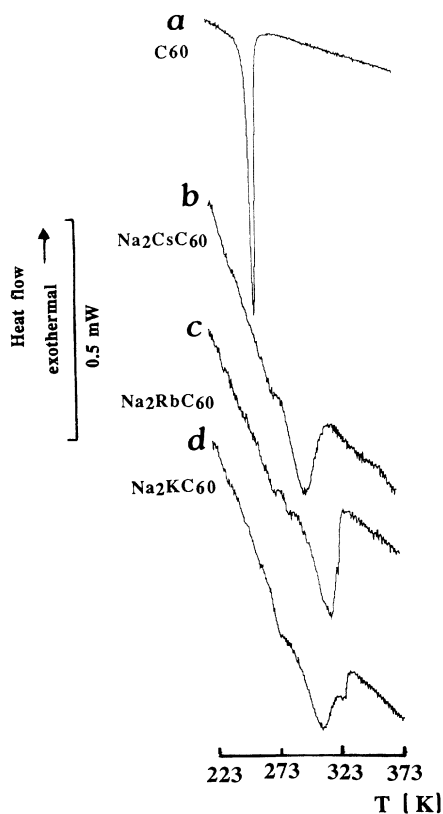


FIG. 2. The endothermic DSC peaks for $\text{Na}_2\text{AC}_{60}$ ($A = \text{Cs, Rb, and K}$) indicating the transitions from rotationally ordered sc to disordered fcc.

450 K. Combining these results to the reported structural and dynamical properties of $\text{Na}_2\text{RbC}_{60}$ (Refs. 8, 10, 12, and 28), $\text{Na}_2\text{CsC}_{60}$ (Ref. 13), and $\text{Na}_2\text{KC}_{60}$ in the present work, we can assign these endothermic heat absorptions to the ordered sc to disordered fcc phase transition. It is very interesting to note that all the $\text{Na}_2\text{AC}_{60}$ compounds show such sc-fcc phase transition reminiscent of pristine C_{60} . This feature is in strong contrast to those of the other superconducting $A_3\text{C}_{60}$'s, such as K_3C_{60} and Rb_3C_{60} , where the structure remains fcc even at low temperatures.^{29,30} Considering that all $\text{Na}_2\text{AC}_{60}$ show the sc-fcc phase transition, the stability of the sc crystal phase in $A_3\text{C}_{60}$ seems to be controlled by the tetrahedral Na^+ with the little influence of the A^+ cation in the octahedral sites.

The details of the sc-fcc phase transition in pristine C_{60} have already been reported.¹⁴⁻²⁷ Our DSC analyses of the pristine C_{60} under ambient pressure are shown for comparison in Fig. 2(a), and show that $T_{\text{sc-fcc}}$ occurs around 255 K with ΔH of ca. 9 J/g, in good agreement with earlier reports.¹⁴⁻²⁷ Higher pressure experiments on pristine C_{60} show that the $T_{\text{sc-fcc}}$ value increases with pressure,³¹ and accordingly with the reduction in lattice parameter. In Fig. 3 the relationship between a_0 and $T_{\text{sc-fcc}}$ under high pressure [here the a_0 values under high pressure are estimated using the reported axial compressibility of $k_\alpha = d \ln a_0 / dp = 1.83 \times 10^{-3} \text{ kbar}^{-1}$ (Refs. 32 and 33)] is plotted together with data for $\text{Na}_2\text{CsC}_{60}$, $\text{Na}_2\text{RbC}_{60}$, and $\text{Na}_2\text{KC}_{60}$ obtained in this work for comparison. The $T_{\text{sc-fcc}}$ value of $\text{Na}_2\text{RbC}_{60}$, which has the smallest lattice parameter among the $\text{Na}_2\text{AC}_{60}$ superconducting family,³⁴ lies on the general curve of $T_{\text{sc-fcc}}$ vs a_0 obtained from pristine C_{60} under high pressure, while those of $\text{Na}_2\text{CsC}_{60}$ and $\text{Na}_2\text{KC}_{60}$ lie above the curve.

In the ordered sc $A_3\text{C}_{60}$ phase, in contrast with pristine C_{60} , the stabilization energy is considered to be gen-

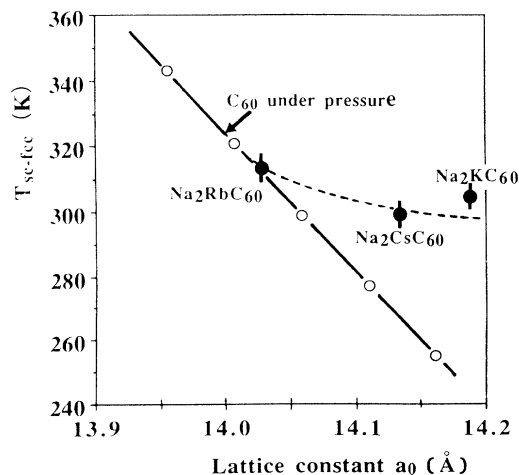


FIG. 3. The relationship between $T_{\text{sc-fcc}}$ and lattice parameter a_0 . The lattice parameters obtained from the diffractions measured at room temperature are used. The dependence of a_0 on temperature will not make a large difference for the purpose of the comparison in this study.

erally determined by both the $C_{60}^{3-}-C_{60}^{3-}$ and $C_{60}^{3-}-A^+$ interactions, where the $C_{60}^{3-}-A^+$ Coulombic interactions work as a secondary effect to stabilize the sc phase.³⁴ It was also pointed out that the short-range repulsive interaction potentials do not favor the sc crystal phase^{30,34} from the calculations on Na_xC_{60} ($x=2$). This can be compared to that for the pristine C_{60} , where only the $C_{60}-C_{60}$ intermolecular interactions are important for the sc phase stability.

If we follow this simple picture, in the small lattice parameter region, the contribution of the $C_{60}^{3-}-C_{60}^{3-}$ interaction would be the main factor controlling T_{sc-fcc} and, accordingly, the T_{sc-fcc} values of Na_2AC_{60} will be close to that of pristine C_{60} under pressure. However in the large lattice parameter region, the $C_{60}^{3-}-A^+$ interaction will also have an effective contribution. The discrepancies observed for Na_2CsC_{60} and Na_2KC_{60} can be considered to be due to this additional effect. Considering the ionic radii of alkali metals, one would have expected that the lattice parameters will be in the order of $a_0(Na_2CsC_{60}) > a_0(Na_2RbC_{60}) > a_0(Na_2KC_{60})$. However, as can be seen in Fig. 3 Na_2KC_{60} does not fit this trend. This has been discussed elsewhere.^{9,35}

The observed ΔH (~ 3 J/g) for Na_2AC_{60} is about one third that of pristine C_{60} . This is in good accord with the values found for Na_xC_{60} ($x=1-2$).³⁴ The recent neu-

tron scattering study on Na_2CsC_{60} showed that the degree of the C-C bond alternation of pentagon-hexagon (5:6) and hexagon-hexagon (6:6) type bonds tends to be reduced compared to that in pristine C_{60} .¹³ This might cause the potential valleys in the $Pa\bar{3}$ sc phase (the 22° and the other two rotations around 82°) to become shallow because of a reduction in the *ad hoc* electrostatic contribution.³⁶⁻³⁸ Accordingly, this will lead to the reduction in ΔH . Another explanation for the smaller ΔH (sc-fcc) observed for Na_2AC_{60} would be the smaller entropy associated with the C_{60}^{3-} orientational fluctuations due to the influence of tetrahedral A^+ than that in the pristine C_{60} having quasi-free rotational characteristics in the high temperature fcc phase.³⁴

It is now clear that all Na_2AC_{60} ($A=Cs, Rb, \text{ and } K$) undergo first-order-like phase transition from fcc to sc at low temperatures. However further studies are still needed to understand the details in lattice parameter and the anomalous low T_c of some of sodium containing fullerenes.

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- ¹R. C. Haddon, A. F. Hebard, M. J. Rosseinsky, D. W. Murphy, S. J. Duclos, K. B. Lyons, B. Miller, J. M. Rosamilia, R. M. Fleming, A. R. Kortan, S. H. Glarum, A. V. Makhijia, A. J. Muller, R. H. Elick, S. M. Zahurak, R. Tycko, G. Dabbagh, and F. A. Thiel, *Nature* **350**, 320 (1991).
- ²A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, *Nature* **350**, 600 (1991).
- ³M. J. Rosseinsky, A. P. Ramirez, S. H. Glarum, D. W. Murphy, R. C. Haddon, A. F. Hebard, T. T. M. Palstra, A. R. Kortan, S. M. Zahurak, and A. V. Makhijia, *Phys. Rev. Lett.* **66**, 2830 (1991).
- ⁴K. Holzer, O. Klein, S.-M. Huang, R. B. Kaner, K. J. Fu, R. L. Whetten, and F. Diederich, *Science* **252**, 1154 (1991).
- ⁵K. Tanigaki, T. W. Ebbesen, S. Saito, J. Mizuki, J. S. Tsai, Y. Shimakawa, Y. Kubo, and S. Kuroshiima, *Nature* **352**, 222 (1991).
- ⁶M. Schluter, M. Lannoo, M. Needels, G. A. Baraff, and D. Tomanek, *Phys. Rev. Lett.* **68**, 526 (1992).
- ⁷R. M. Fleming, A. P. Ramirez, M. J. Rosseinsky, D. W. Murphy, R. C. Haddon, S. M. Zahurak, and A. V. Makhijia, *Nature* **352**, 787 (1991).
- ⁸K. Tanigaki, I. Hiroseawa, T. W. Ebbesen, J. Mizuki, Y. Shimakawa, Y. Kubo, J. S. Tsai, and S. Kuroshima, *Nature* **356**, 419 (1992).
- ⁹M. J. Rosseinsky, D. W. Murphy, R. M. Fleming, R. Tycko, A. P. Ramirez, T. Siegrist, G. Dabbagh, and S. E. Barrett, *Nature* **356**, 416 (1992).
- ¹⁰K. Tanigaki, T. W. Ebbesen, J.-S. Tsai, I. Hiroseawa, and J. Mizuki, *Europhys. Lett.* **23**, 57 (1993).
- ¹¹K. Tanigaki, I. Hiroseawa, T. W. Ebbesen, and J. Mizuki, *J. Phys. Chem. Solids* **54**, 1645 (1993).
- ¹²K. Kniaz, J. E. Fischer, Q. Zhu, M. J. Rosseinsky, O. Zhou, and D. W. Murphy, *Solid State Commun.* **88**, 47 (1993).
- ¹³Kosmas, C. Christides, I. M. Thomas, J. Mizuki, K. Tanigaki, I. Hiroseawa, and T. W. Ebbesen, *Science* **263**, 950 (1994).
- ¹⁴A. Dworkin, H. Szwarc, S. Leach, J. P. Hare, T. J. Dennis, H. W. Kroto, R. Taylor, and D. R. M. Walton, *C. R. Acad. Sci. Ser. II* **312**, 979 (1991).
- ¹⁵P. A. Heiney, J. E. Fischer, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley Jr., A. B. Smith III, and D. E. Cox, *Phys. Rev. Lett.* **66**, 2911 (1991).
- ¹⁶J. R. D. Copleym, D. A. Neumann, R. L. Cappelletti, W. A. Kamitakahara, E. Prince, N. Coustel, J. P. McCauley Jr., N. C. Maliszewsky, J. E. Fischer, A. B. Smith III, K. M. Creegan, and D. M. Cox, *Physica B* **180&181**, 706 (1992).
- ¹⁷R. Sachidanandam and A. B. Harris, *Phys. Rev. Lett.* **67**, 1467 (1991).
- ¹⁸A. B. Harris and R. Sachidanandam, *Phys. Rev. B* **46**, 4944 (1992).
- ¹⁹P. A. Heiney, J. E. Fischer, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley Jr., A. B. Smith III, and D. E. Cox, *Phys. Rev. Lett.* **67**, 1468 (1991).
- ²⁰S. Liu, Y. J. Lu, M. M. Kappes, and J. A. Ibers, *Science* **254**, 408 (1991).
- ²¹R. Moret, S. Ravy, and J.-M. Godard, *J. Phys. I. (France)* **2**, 1699 (1992).
- ²²W. I. F. David, R. M. Ibberson, J. C. Matthewman, K. Prassides, T. J. Dennis, J. P. Hare, H. W. Kroto, T. Taylor, and D. R. M. Walton, *Nature* **353**, 147 (1991).
- ²³K. Prassides, H. W. Kroto, R. Taylor, D. R. M. Walton, W. I. F. David, J. Tomkinson, M. J. Rosseinsky, D. W. Murphy, and R. C. Haddon, *Carbon* **30**, 1277 (1993).
- ²⁴J. R. D. Copley, D. A. Neuman, R. L. Cappelletti, and W. A.

- Kamitakahara, *J. Phys. Chem. Solids* **53**, 1353 (1992).
- ²⁵N. Yao, C. F. Klein, S. K. Bahal, M. M. Disko, R. D. Sherwood, and D. M. Cox, *Phys. Rev. B* **45**, 11 366 (1992).
- ²⁶G. van Tendeloo, S. Amelinckx, M. A. Verheijen, P. H. M. van Loosdrecht, and G. Meijer, *Phys. Rev. Lett.* **69**, 1065 (1992).
- ²⁷C. Christides, D. A. Neuman, K. Prassides, J. R. D. Copley, J. J. Rush, M. J. Rosseinsky, D. W. Murphy, and R. C. Haddon, *Phys. Rev. B* **46**, 12 088 (1992).
- ²⁸C. Christides, K. Prassides, D. A. Neumann, J. R. D. Copley, J. Mizuki, K. Tanigaki, I. Hirose, and T. W. Ebbesen, *Europhys. Lett.* **24**, 755 (1993).
- ²⁹P. Stephens, L. Mihaly, P. L. Lee, R. L. Whetten, S.-M. Huang, R. Kaner, F. Deiderich, and K. Holczer, *Nature* **351**, 632 (1991).
- ³⁰J. Fischer and P. A. Heiney, *J. Phys. Chem. Solids* (to be published).
- ³¹G. A. Samara, J. E. Schirber, B. Morosin, L. V. Hansen, D. Loy, and A. P. Sylwester, *Phys. Rev. Lett.* **67**, 3136 (1991).
- ³²J. E. Fischer, P. A. Heiney, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley Jr., and A. B. Smith III, *Science* **152**, 1288 (1991).
- ³³S. J. Duclos, K. Brister, R. C. Haddon, A. R. Kortan, and F. A. Thiel, *Nature* **351**, 380 (1991).
- ³⁴T. Yildirim, J. E. Fischer, A. B. Harris, P. W. Stephens, D. Liu, L. Bard, R. A. Strongin, and A. B. Smith III, *Phys. Rev. Lett.* **71**, 1383 (1993).
- ³⁵K. Tanigaki *et al.*, *Chem. Phys. Lett.* **213**, 395 (1993).
- ³⁶L. P. Lu, X.-P. Li, and R. M. Martin, *Phys. Rev. Lett.* **68**, 1551 (1992).
- ³⁷M. Spirk, A. Cheng, and M. L. Klein, *J. Phys. Chem.* **96**, 2027 (1992).
- ³⁸J. E. Schirber, D. L. Overmyer, W. R. Bayless, M. J. Rosseinsky, O. Zhou, D. W. Murphy, Q. Zhu, K. Kniaz, and J. E. Fischer, *J. Phys. Chem. Solids* (to be published).