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## Metal-insulator transition at 50 K in $\text{Na}_2\text{C}_{60}$

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Temperature dependence of electron spin resonance in  $\text{Na}_2\text{C}_{60}$  was studied in a temperature range from 2 to 350 K. It was shown that  $\text{Na}_2\text{C}_{60}$  was metallic above 50 K and had a metal-insulator transition at 50 K. The center frequency for the Hg(2) Raman mode in  $\text{Na}_2\text{C}_{60}$  at 298 K was close to those in the metallic  $\text{Rb}_3\text{C}_{60}$ ,  $\text{K}_3\text{C}_{60}$ , and  $\text{Cs}_3\text{C}_{60}$ , while the linewidth was close to that in the metallic but nonsuperconducting  $\text{Cs}_3\text{C}_{60}$ . The Hg(2) mode showed a large blueshift and narrowing at 50 K. The center frequency and the linewidth in the low-temperature region from 50 K were almost the same as those in the insulating  $\text{C}_{60}$  and  $\text{Rb}_6\text{C}_{60}$ , which showed the metal-insulator transition at 50 K in  $\text{Na}_2\text{C}_{60}$ . The origin of this metal-insulator transition was discussed in terms of the electron-phonon interaction (Jahn-Teller effect) and the electron-electron interaction (Mott-Hubbard picture). [S0163-1829(99)04123-5]

### INTRODUCTION

The structure and physical properties of Na-doped  $\text{C}_{60}$  ( $\text{Na}_x\text{C}_{60}$ ) are of very interest because they are different from those of the other alkali-doped  $\text{C}_{60}$  ( $A_x\text{C}_{60}$ ,  $A$ :K, Rb, and Cs).<sup>1-7</sup> The superconducting phase has not yet been found for  $\text{Na}_x\text{C}_{60}$ ;  $\text{Na}_3\text{C}_{60}$ , which exhibits an face-centered cubic (fcc) structure ( $Fm\bar{3}m$ ) is not a superconductor,<sup>1</sup> contrary to  $\text{Rb}_3\text{C}_{60}$  and  $\text{K}_3\text{C}_{60}$ .  $\text{Na}_x\text{C}_{60}$  with  $x > 6$  can exist because of a small ionic radius of  $\text{Na}^+$  ion; Yildirim *et al.* prepared  $\text{Na}_{9.7}\text{C}_{60}$  with an fcc structure ( $Fm\bar{3}$ ).<sup>2</sup> Recently, Oszlanyi *et al.* succeeded in preparing and characterizing  $\text{Na}_4\text{C}_{60}$  with two-dimensional polymer structure ( $I2/m$ ); the  $\text{C}_{60}$  molecules were connected with "single" bonds.<sup>3</sup> The structure is different from that of  $A_4\text{C}_{60}$ , which takes a body-centered tetragonal (bct) ( $I4/mmm$ ) (Ref. 8) or a body-centered orthorhombic (bco) structure ( $Immm$ ).<sup>9</sup> In addition to these phases of  $\text{Na}_x\text{C}_{60}$ , the existence of two stable phases with an fcc structure ( $Fm\bar{3}m$ ) is confirmed, which are  $\text{Na}_2\text{C}_{60}$  and  $\text{Na}_6\text{C}_{60}$ .<sup>1,4</sup> The structure of  $\text{Na}_6\text{C}_{60}$  is different from a body-centered cubic (bcc) structure ( $Im\bar{3}$ ) for  $A_6\text{C}_{60}$ .<sup>1,8</sup> Furthermore, we recently reported the existence of  $\text{NaC}_{60}$  with an fcc structure.<sup>5</sup>

Early studies on the physical properties of  $\text{Na}_x\text{C}_{60}$  showed that these are insulating,<sup>10,11</sup> except for one that reported a metallic behavior for  $\text{Na}_2\text{C}_{60}$  from the photoemission spectra.<sup>12</sup> Recently, Yildirim *et al.* reported the metallic behavior for  $\text{Na}_6\text{C}_{60}$  in the temperature region from 100 to 300 K on the basis of the spin susceptibility  $\chi_{\text{spin}}$  determined from electron spin resonance (ESR).<sup>6</sup> The polymeric phase of  $\text{Na}_4\text{C}_{60}$  also exhibited the metallic behavior.<sup>3</sup> The  $\chi_{\text{spin}}$  of

$\text{Na}_4\text{C}_{60}$  ( $1.7 \times 10^{-4} \text{ emu mol}^{-1}$ ) was smaller than that of  $\text{RbC}_{60}$  ( $8 \times 10^{-4} \text{ emu mol}^{-1}$ ),<sup>3</sup> suggesting a large bandwidth of  $\text{Na}_4\text{C}_{60}$ . Further, the high-temperature phase of  $\text{Na}_4\text{C}_{60}$  was metallic contrary to  $A_4\text{C}_{60}$ , although the phase took the same structure (bct,  $I4/mmm$ ) as  $A_4\text{C}_{60}$ .<sup>7</sup> The difference was rationalized on the basis of the Mott-Hubbard picture.<sup>7,13</sup>

In the present paper, we report the metallic behavior of  $\text{Na}_2\text{C}_{60}$  and a metal-insulator (M-I) transition at 50 K on the basis of temperature-dependent ESR and Raman scattering. To our knowledge, this is the first experimental evidence for the M-I transition in  $\text{Na}_2\text{C}_{60}$ . Further, the electron-phonon coupling in  $\text{Na}_2\text{C}_{60}$  evaluated from Raman scattering is discussed in order to approach the origin of the M-I transition.

### EXPERIMENT

The  $\text{Na}_2\text{C}_{60}$  sample was prepared by annealing stoichiometric amounts of  $\text{C}_{60}$  and Na metal for 856 h at 723 K under  $10^{-3}$  Torr; a trace of benzene was removed before annealing. The nominal value of Na was 2.6. The sample was introduced into a quartz capillary tube for Raman and x-ray diffraction measurements, and an ESR tube for ESR and electron spin echo (ESE) measurements. The temperature-dependent ESR and ESE spectra were recorded at an x-band ESR spectrometer (Bruker ESP300) and Pulse Fourier-transform ESR spectrometer (Bruker ESP380E), respectively, equipped with an Oxford He flow Cryostat (ESR910). The temperature-dependent Raman spectra were measured by using an ISA Confocal LABRAM System equipped with an Oxford He flow Cryostat (Microstat-He) at an excitation of 632.8 nm with He-Ne laser: the spectral resolution was  $5.0 \text{ cm}^{-1}$ . The x-ray diffraction pattern was

measured with synchrotron radiation of  $\lambda = 1.1010 \text{ \AA}$  at the BL-6C in the Photon Factory of High-Energy Accelerator Research Organization (KEK-PF). The differential scanning calorimetry (DSC) curve was recorded at the heating and cooling rates of  $10 \text{ K min}^{-1}$  with a Perkin-Elmer DSC7 calorimeter.

## RESULTS

The Ag(2) Raman peak for the sample at 298 K showed the center frequency  $\omega_0$  of  $1461 \text{ cm}^{-1}$ . Comparison of the  $\omega_0$  with that reported for Na<sub>x</sub>C<sub>60</sub> (Ref. 14) showed that this sample was Na<sub>2</sub>C<sub>60</sub>. The x-ray diffraction pattern at 298 K showed the same pattern as that for Na<sub>2</sub>C<sub>60</sub> reported previously.<sup>4</sup> The pattern was assigned to a simple cubic structure ( $Pa\bar{3}$ ) and the lattice constant  $a$  was  $14.19(1) \text{ \AA}$ , consistent with that reported previously,  $14.184 \text{ \AA}$ .<sup>4</sup> The  $a$  for Na<sub>2</sub>C<sub>60</sub> was close to that for C<sub>60</sub> ( $14.17 \text{ \AA}$ ).<sup>15</sup> The Rietveld analysis showed that the x-ray diffraction pattern could be reproduced with the atomic coordinates for the pristine C<sub>60</sub> at 5 K (Ref. 16) and  $x = 0.236(6)$  for the Na atom on  $8c$  site ( $x, x, x$ ). The orientation of C<sub>60</sub> in Na<sub>2</sub>C<sub>60</sub> determined in the present analysis was the same as that reported by Yildirim *et al.*<sup>4</sup> The  $x$  value was close to that for Na<sub>2</sub>CsC<sub>60</sub> ( $x = 0.241$ ).<sup>17</sup> This fact showed that the intercalation of Cs atom into  $4b$  site ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ) little affected to the position of Na atom on the  $8c$  site. The DSC curve exhibited an endothermic peak at 325 K in a heating process. This peak can be assigned to the phase transition from the low-temperature simple cubic phase to the high-temperature fcc phase in Na<sub>2</sub>C<sub>60</sub>, as was reported by Yildirim *et al.*<sup>4</sup> and Khairullin, Chang, and Hwang.<sup>18</sup> No peaks except for this peak were observed in the DSC curve. These results showed that the sample was a single phase of Na<sub>2</sub>C<sub>60</sub>.

Figures 1(a), 1(b), and 1(c) show the ESR spectra for Na<sub>2</sub>C<sub>60</sub> at 295 and 2 K, and the ESE spectrum observed in the field scan at 20 K, respectively. The spectrum at 295 K could be reproduced by using two Lorentzian functions with the peak-to-peak line widths  $\Delta H_{pp}$  of 11.5 and 2.1 G. The spectrum was similar to that of NaC<sub>60</sub>, which was composed of two components with  $\Delta H_{pp}$  of 12.6 and 2.0 G at 263 K.<sup>5</sup> These parameters were determined by a least-squares fitting with two Lorentzian functions. The ESR spectra were measured in a cooling process from 295 to 2 K, and in a heating process from 295 to 350 K. The ESE spectrum shown in Fig. 1(c) exhibited clearly the existence of two components with half linewidths  $\Delta H_{1/2} (= \sqrt{3} \Delta H_{pp})$  of 11.6 and 4.9 G; the  $\Delta H_{pp}$  of 6.7 and 2.9 G were consistent with those evaluated from ESR [Fig. 3(a)]. This result shows that the ESR spectrum should be analyzed by two components. The spectrum for Na<sub>2</sub>C<sub>60</sub> at 2 K was also composed of two Lorentzian functions with  $\Delta H_{pp}$  of 5.1 and 1.6 G.

As seen from Fig. 2(a), the temperature dependence of the  $\chi_{\text{spin}}$  for the narrow component could be reproduced by Curie plus Pauli contributions; the Curie constant and  $\chi_{\text{spin}}$  of the Pauli-type contribution were  $1.60 \times 10^{-3} \text{ emu K mol}^{-1}$  and  $0.424 \times 10^{-4} \text{ emu mol}^{-1}$ , respectively. The Curie contribution was attributed to the paramagnetic defects in the crystals, as done for NaC<sub>60</sub>.<sup>5</sup> However, the origin of the small Pauli contribution found from the narrow ESR component was not clarified. As seen from Fig. 2(b), the broad compo-

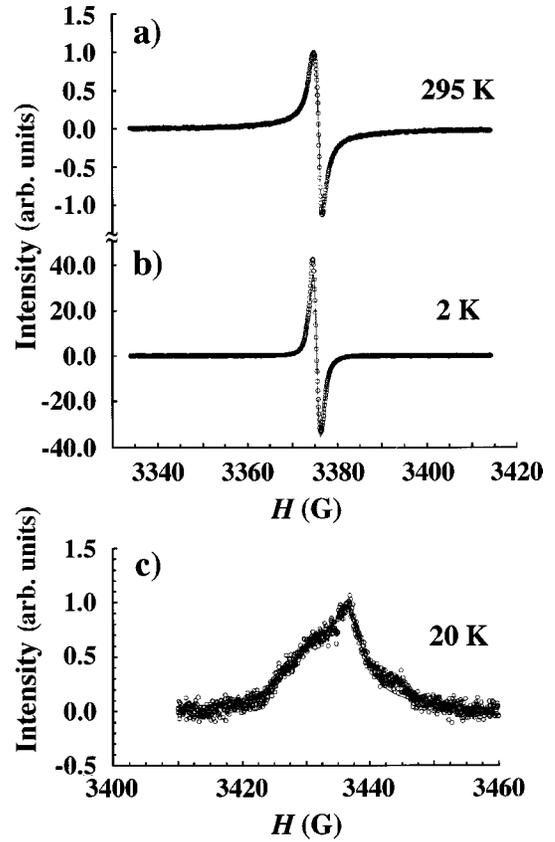


FIG. 1. ESR spectra of Na<sub>2</sub>C<sub>60</sub> at (a) 295 and (b) 2 K. (c) ESE spectrum of Na<sub>2</sub>C<sub>60</sub> at 20 K recorded in the field scan. The open circles and the solid lines refer to the experimental and the best-fitted spectra, respectively.

nent showed a Pauli-like behavior between 50 and 300 K, as a conventional metal. The  $\chi_{\text{spin}}$  of the broad component decreased abruptly in the temperature region from 50 K. This change suggests the M-I transition at 50 K. The small decrease in the  $\chi_{\text{spin}}$  of the narrow component between 20 and 50 K shown in Fig. 2(a) seems to be apparently observed owing to an abrupt decrease in the broad component. The  $\chi_{\text{spin}}$  evaluated from the broad component was  $1.3 \times 10^{-4} \text{ emu mol}^{-1}$  at 295 K, which was smaller than those for Rb<sub>3</sub>C<sub>60</sub> ( $12.7 \times 10^{-4} \text{ emu mol}^{-1}$ ),<sup>19</sup> K<sub>3</sub>C<sub>60</sub> ( $9.3 \times 10^{-4} \text{ emu mol}^{-1}$ ) (Ref. 19) and Cs<sub>3</sub>C<sub>60</sub> ( $6.0 \times 10^{-4} \text{ emu mol}^{-1}$ ).<sup>20,21</sup> The  $\chi_{\text{spin}}$  of  $1.3 \times 10^{-4} \text{ emu mol}^{-1}$  was consistent with that for Na<sub>2</sub>C<sub>60</sub> at 290 K reported by Iwasa (ca.  $1.5 \times 10^{-4} \text{ emu mol}^{-1}$ ).<sup>22</sup> Further, the  $\chi_{\text{spin}}$  was close to that for the polymeric Na<sub>4</sub>C<sub>60</sub> at 300 K ( $1.7 \times 10^{-4} \text{ emu mol}^{-1}$ ) and was a little smaller than that for the monomeric Na<sub>4</sub>C<sub>60</sub> (ca.  $4.0 \times 10^{-4} \text{ emu mol}^{-1}$ ).<sup>3,7</sup> The density of state  $N(\varepsilon_F)$  on the Fermi level in Na<sub>2</sub>C<sub>60</sub> was evaluated to be 2 state/eV-spin-C<sub>60</sub>, which was smaller than those for Rb<sub>3</sub>C<sub>60</sub> (19 state/eV-spin-C<sub>60</sub>),<sup>19</sup> K<sub>3</sub>C<sub>60</sub> (14 state/eV-spin-C<sub>60</sub>),<sup>19</sup> and Cs<sub>3</sub>C<sub>60</sub> (9 state/eV-spin-C<sub>60</sub>).<sup>21</sup> The small  $N(\varepsilon_F)$  suggests that the bandwidth  $W$  in the conduction band is larger for Na<sub>2</sub>C<sub>60</sub> than those for Rb<sub>3</sub>C<sub>60</sub>, K<sub>3</sub>C<sub>60</sub>, and Cs<sub>3</sub>C<sub>60</sub>. The large  $W$  can reasonably be explained by the small  $a$  in Na<sub>2</sub>C<sub>60</sub>.

The sum of the  $\chi_{\text{spin}}$  of two components shown in Fig. 2(c) exhibited an abrupt increase with a decrease in temperature at low temperatures because of the Curie-type contribu-

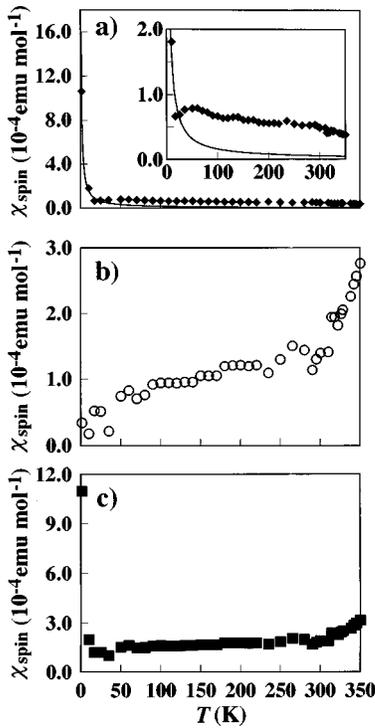


FIG. 2. Temperature dependence of the  $\chi_{\text{spin}}$  evaluated from (a) the narrow ESR component, (b) the broad component, and (c) the sum of the broad and narrow components. The solid line in (a) shows the Curie contribution in the narrow component. The inset in (a) shows the  $\chi_{\text{spin}}$  for the narrow components except for that at 2 K.

tion. A small decrease found between 20 and 50 K originates from an abrupt decrease in the  $\chi_{\text{spin}}$  of the broad component. Though the total  $\chi_{\text{spin}}$  for  $\text{Na}_2\text{C}_{60}$  reported by Iwasa showed the Curie-like behavior,<sup>22</sup> the total  $\chi_{\text{spin}}$  determined in the present study suggested the existence of some components other than the Curie-type component. The total  $\chi_{\text{spin}}$  for  $\text{Na}_2\text{C}_{60}$  reported by Petit *et al.* showed the Curie-Weiss behavior (the Weiss temperature  $\theta = 12$  K), and a drastic de-

crease below 10 K, which was assigned to the antiferromagnetic state.<sup>23</sup> As seen from Fig. 2(c), such a drastic decrease was not observed, though a small decrease in  $\chi_{\text{spin}}$  was observed from 20 to 50 K. The  $\chi_{\text{spin}}$  above 300 K showed an abrupt increase, which was consistent with the result reported by Petit *et al.*<sup>23</sup> They pointed out that the increase was caused by a singlet-triplet equilibrium of the spin states of  $\text{C}_{60}^{2-}$  dianion in  $\text{Na}_2\text{C}_{60}$ .<sup>23</sup> As seen from Figs. 2(a) and (b), the  $\chi_{\text{spin}}$  of the broad component increased abruptly above 300 K, while the narrow component did not show such an increase. The fact suggests that the narrow component does not originate from the spin state of  $\text{Na}_2\text{C}_{60}$ .

As seen from Fig. 3(a), the  $\Delta H_{pp}$  for the narrow component was almost constant below 300 K, while the component broadened slightly above 300 K. The  $\Delta H_{pp}$  for the broad component was almost constant above 50 K, and decreased abruptly in the low-temperature region from 50 K. The results are very similar to those for  $\text{NaC}_{60}$ , except for the difference in the transition temperature: 280 K for  $\text{NaC}_{60}$ .<sup>5</sup> The  $g$  factors for the narrow and broad components are shown in Fig. 3(b). The  $g$  factor for the narrow component was almost constant, while that for the broad component decreased below 50 K, suggesting the transition at 50 K. It was supported from the temperature dependence of the  $\Delta H_{pp}$  and the  $g$  factor that the narrow component could primarily be attributed to the paramagnetic defects. The  $\Delta H_{pp}$  for the broad component did not show a linear decrease with a decrease in temperature, as is expected for the conventional metal  $\text{Rb}_3\text{C}_{60}$ , which was metallic in the normal state above the superconducting transition temperature, showed an increase in  $\Delta H_{pp}$  with decreasing temperature.<sup>24</sup> The peculiar temperature dependence of  $\Delta H_{pp}$  was controversial because it was different from that in the conventional metal. Furthermore, the quadratic temperature dependence of the electric resistivity, which is closely associated with that of  $\Delta H_{pp}$ , was also controversially discussed.<sup>25–27</sup> Some proposals were presented based on the electron-electron scattering and the lattice contraction to explain this peculiar temperature dependence.<sup>24–27</sup> However, Petit *et al.* found a decrease in

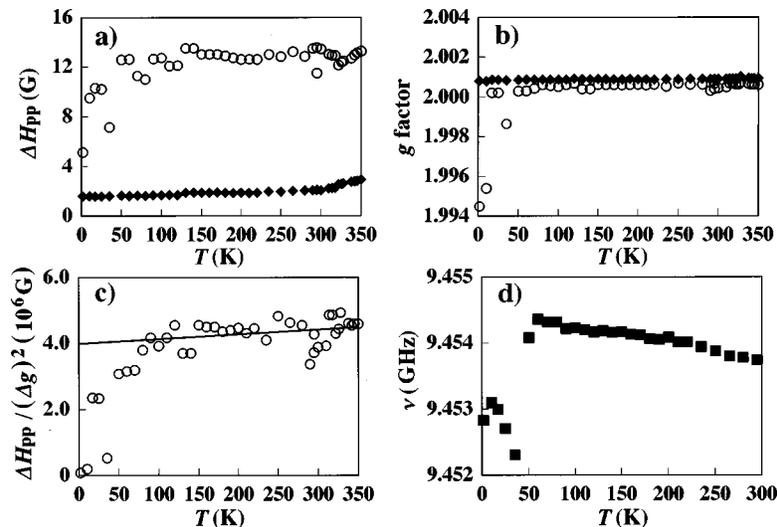


FIG. 3. (a) Temperature dependence of (a) the  $\Delta H_{pp}$  and (b)  $g$  factor. The open circles and the rhombuses refer to the broad and the narrow components, respectively. (c) Temperature dependence of the  $\Delta H_{pp}/(\Delta g)^2$  for the broad component. (d) Temperature dependence of the resonance frequency  $\nu$ .

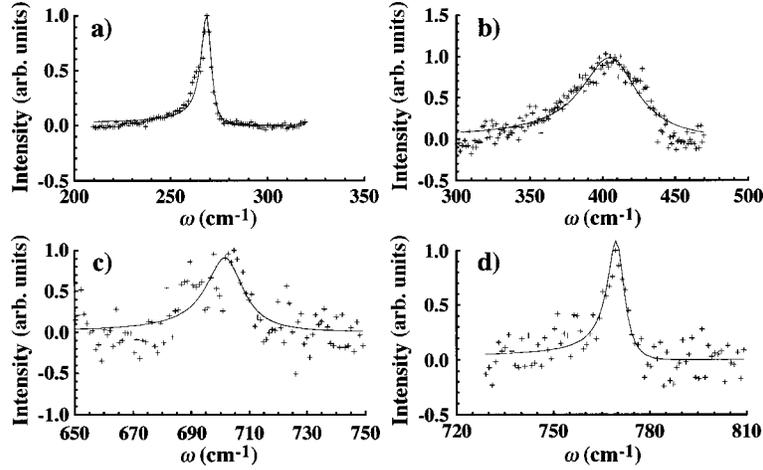


FIG. 4. Raman spectra for (a) the Hg(1), (b) Hg(2), (c) Hg(3), and (d) Hg(4) modes. The crosses and the solid lines refer to the experimental and the best-fitted Raman spectra, respectively. The fitting was carried out based on a single component.

the  $\Delta H_{pp}/(\Delta g)^2$  when decreasing temperature:  $\Delta g = g - 2.0023$ .<sup>28</sup> The results could well be explained by the Elliott-Yafet relation for the conventional metal,<sup>29,30</sup> implying that Rb<sub>3</sub>C<sub>60</sub> was a metal above the superconducting transition.

Figure 3(c) shows the temperature dependence of the  $\Delta H_{pp}/(\Delta g)^2$  in Na<sub>2</sub>C<sub>60</sub> evaluated from the  $\Delta H_{pp}$  [Fig. 3(a)] and the  $g$  factor [Fig. 3(b)] for the broad component. The temperature dependence showed a slight decrease in the  $\Delta H_{pp}/(\Delta g)^2$  with a decrease in temperature above 50 K, suggesting the metallic character of Na<sub>2</sub>C<sub>60</sub>. The result implies that the dominant process for the spin-lattice relaxation in the broad ESR component is caused by the modulation of the spin-orbit interaction due to the lattice vibrations. However, the decrease was observed less clearly than that in Rb<sub>3</sub>C<sub>60</sub>. Consequently, it should also be pointed out that the other effects such as the electron-electron interaction may contribute to the temperature dependence of the  $\Delta H_{pp}$ . The  $\Delta H_{pp}/(\Delta g)^2$  also decreased abruptly in the low-temperature region from 50 K, suggesting the transition of the magnetic states. We have concluded from the Pauli-like  $\chi_{\text{spin}}$  and the decrease in the  $\Delta H_{pp}/(\Delta g)^2$  that Na<sub>2</sub>C<sub>60</sub> is metallic above 50 K, and that the M-I transition occurs at 50 K. The broad component in Na<sub>2</sub>C<sub>60</sub> was assigned to the conduction-electron ESR (c-ESR).

Figure 3(d) shows the temperature dependence of the resonance frequency  $\nu$  in the ESR measurements. The  $\nu$  increased monotonically with decreasing temperature above 50 K. Below 50 K the values decreased drastically. This drastic change reflects the change in the electric conductivity; the  $\nu$  for materials which has no transition increases monotonically with a decrease in temperature. Therefore, the temperature dependence of the  $\nu$  also supports the M-I transition in Na<sub>2</sub>C<sub>60</sub> around 50 K.

Figures 4(a), 4(b), 4(c), and 4(d) show the Raman spectra for the Hg(1), Hg(2), Hg(3), and Hg(4) observed at 298 K. The center frequency  $\omega_0$ , the width  $\Gamma$ , and the asymmetric parameter  $q$  were determined by a least-squares fitting with Breit-Wigner-Fano formula; the fitting was carried out with a single component. These parameters are collected in Table I, together with those for the Ag(1) and Ag(2). Winter and Kuzmany analyzed the Hg(1) and Hg(2) peaks for a single

crystal of K<sub>3</sub>C<sub>60</sub> by the five-components fitting,<sup>31</sup> because their spectrometer with high-spectral resolution (3 cm<sup>-1</sup>) showed splitting for these peaks. The fitting with the two components was carried out for the Hg(1) peak in Na<sub>2</sub>C<sub>60</sub> since a small additional component was observed. Figures 5(a) and 5(b) show the Hg(1) peaks at 298 and 2 K, respectively, together with the two-components fitting-curves. This two-components fitting led to an improvement in the parameter fitting. The  $\omega_0$ ,  $\Gamma$ , and  $q$  by the fitting are also listed in Table I. The weighted average values of the  $\omega_0$ ,  $\Gamma$ , and  $q$  determined by the two-components fitting were consistent with those by a single-component fitting. The splitting in the Hg(2) peak was not clearly observed because of the spectral resolution of our Raman equipment and the polycrystalline sample. Thus, only a single-component fitting was employed in the analysis for the Hg(2) peak. The  $\omega_0$ ,  $\Gamma$ , and  $q$  determined by a single-component fitting should correspond to the weighted average values for those determined by multi-components fitting.

The  $\Gamma$  for the Hg(2) mode at 298 K was extremely larger than those for the other modes. The  $\Gamma$  for the other modes in Na<sub>2</sub>C<sub>60</sub> were comparable to those in C<sub>60</sub> at room

TABLE I. The values of  $\omega_0$  (cm<sup>-1</sup>),  $\Gamma$  (cm<sup>-1</sup>),  $q$ , and  $\Delta\Gamma/\omega_0^2$  (10<sup>-5</sup> cm) for Raman-active modes at 298 K in Na<sub>2</sub>C<sub>60</sub>. Parameters determined by a single-component fitting.

Mode	Na <sub>2</sub> C <sub>60</sub>				C <sub>60</sub> <sup>a</sup>	
	$\omega_0$	$\Gamma$	$q$	$\Delta\Gamma/\omega_0^2$	$\omega_0$	$\Gamma$
Hg(1)	269	3	-7	}	270	4.2
	269	2	-17			
	263	4	-13			
Hg(2)	406	24	-15	11	430.5	5.5
Ag(1)	492	3	-35	0.06	493	2.5
Hg(3)	702	8	-16	0.06	708	7.5
Hg(4)	770	3	-7		773	9.0
Ag(2)	1461	4	374	0.10	1469	1.5

<sup>a</sup>Parameters at 300 K taken from Ref. 32 (488 and 514.5 nm excitation).

<sup>b</sup>Parameters determined by two-components fitting.

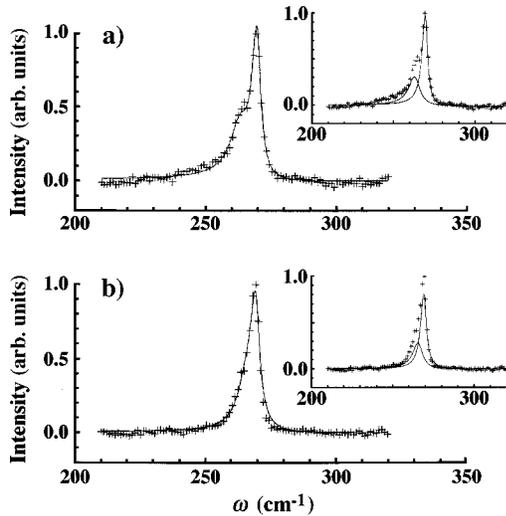


FIG. 5. Raman spectra for the Hg(1) mode at (a) 298 and (b) 2 K. The crosses and the solid lines refer to the experimental and the best-fitted Raman spectra, respectively. The fitting was carried out based on two components. Two components are drawn with the solid line in the inset with the experimental spectrum.

temperature.<sup>21,32</sup> Consequently, it was suggested that the interaction between the electron and intramolecular Hg(2) phonon was very strong. The electron phonon coupling constant  $\lambda$  for the Hg(2) mode was evaluated to be 0.7 from the  $\Delta\Gamma/\omega_0^2$  of  $11.0 \times 10^{-5}$  cm and the  $N(\epsilon_F)$  of 2 state/eV-spin- $C_{60}$  according to  $\lambda_i = C\Delta\Gamma_i/[\omega_{0i}^2 N(\epsilon_F)]$  and  $\Delta\Gamma_i = \Gamma_i(\text{Na}_2\text{C}_{60}) - \Gamma_i(\text{C}_{60})$ ;<sup>33,34</sup> the  $\omega_{0i}$  is the  $\omega_0$  for the  $i$ th Raman mode and  $C = d_i/\pi$ ,  $d_i$  being the degeneracy of the  $i$ th mode ( $d_i = 5$  for Hg mode and  $d_i = 1$  for Ag mode). The  $\Gamma_i(\text{Na}_2\text{C}_{60})$  and  $\Gamma_i(\text{C}_{60})$  are the linewidth  $\Gamma$  for the  $i$ th mode in  $\text{Na}_2\text{C}_{60}$  and  $\text{C}_{60}$ , respectively. The total  $\lambda (= \sum \lambda_i)$  was 0.7, which was comparable to that in  $\text{Rb}_3\text{C}_{60}$  at room temperature ( $\lambda = 0.5$ ).<sup>32</sup> The total  $\lambda$  in  $\text{Na}_2\text{C}_{60}$  is primarily contributed from the Hg(2) mode.

The  $1/q$  implies the strength of the coupling between the continuum and the discrete modes. If the continuum is assigned to the electronic origin rather than vibrational, the  $1/q$  can become a measure of the coupling strength of each mode with the electrons which participate in the electronic transition.<sup>32,35</sup> The origin of the continuum around Hg(2) in  $\text{Rb}_3\text{C}_{60}$  was assigned to the interband  $t_{1u} - t_{1u}^*$  transitions.<sup>32,35</sup> The three degenerate  $t_{1u}$  orbitals in  $\text{C}_{60}$  form the conduction band, and the transition energy of the interband  $t_{1u} - t_{1u}^*$  was expected to be as small as 0.1 eV from the band-structure calculation,<sup>36</sup> so that the interband transition can be excited by the Hg(2) Raman scattering process. Therefore, the  $1/q$  for the Hg(2) mode is a measure of the coupling to the  $t_{1u}$  conduction electrons. The  $1/q$  of  $-0.07$  for the Hg(2) mode at 298 K suggests the intense coupling. Further, the negative value of  $1/q$  implies that the  $\omega_0$  for the electronic continuum lies below the  $\omega_0$  for the Hg(2) mode.

Figures 6(a), 6(b), and 6(c) show the the Raman spectra for the Hg(1), Hg(2), and Hg(4) observed at 2 K. The clear blueshift of  $\omega_0$  and the narrowing in  $\Gamma$  for the Hg(2) peak at 2 K can be found in comparison with those at 298 K. On the other hand, the clear changes were not observed for the Hg(1) and Hg(4) peaks. The  $\omega_0$ ,  $\Gamma$ , and  $q$  for the Hg and Ag

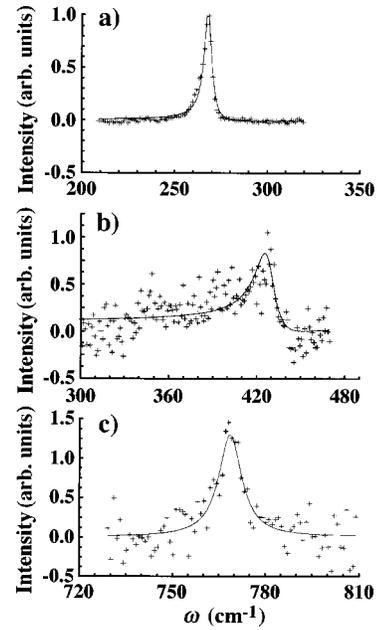


FIG. 6. Raman spectra for (a) the Hg(1), (b) Hg(2), and (c) Hg(4) modes. The crosses and the solid lines refer to the experimental and the best-fitted Raman spectra, respectively. The fitting was carried out based on a single component.

modes at 2 K are listed in Table II. Figures 7(a), 7(b), and 7(c) show the temperature dependence of the  $\omega_0$ ,  $\Gamma$ , and  $q$  for the Hg(2) mode in  $\text{Na}_2\text{C}_{60}$ . The  $\omega_0$  showed a drastic blueshift at 50 K; the  $\omega_0$  was approximately  $410 \text{ cm}^{-1}$  above 70 K, while the  $\omega_0$  approximately  $430 \text{ cm}^{-1}$  at 50 K and the temperatures lower than 50 K. The  $\omega_0$  above 70 K is close to those observed at room temperatures for  $\text{Rb}_3\text{C}_{60}$  ( $395 \text{ cm}^{-1}$  at 300 K,<sup>32</sup>  $408 \text{ cm}^{-1}$  at 300 K),<sup>37</sup>  $\text{K}_3\text{C}_{60}$  ( $416 \text{ cm}^{-1}$  at 300 K),<sup>32</sup> and  $\text{Cs}_3\text{C}_{60}$  ( $406 \text{ cm}^{-1}$  at 290 K),<sup>21</sup> which show the metallic behavior; the excitation wavelengths were 488 and 514.5 nm for Refs. 32 and 37, and 632.8 nm for Ref. 21. The  $\omega_0$  for the Hg(2) mode observed by 1064 nm excitation were  $435 \text{ cm}^{-1}$  for  $\text{Rb}_3\text{C}_{60}$  and  $430 \text{ cm}^{-1}$  for  $\text{K}_3\text{C}_{60}$  (Ref. 35), which were largely different from those by 488 or 514.5 nm excitation.<sup>35</sup> The difference seems to originate from the large difference in the excitation wavelength. Consequently, the  $\omega_0$  for  $\text{Na}_2\text{C}_{60}$  obtained by 632.8 nm excitation cannot di-

TABLE II. The values of  $\omega_0$  ( $\text{cm}^{-1}$ ),  $\Gamma$  ( $\text{cm}^{-1}$ ), and  $q$  for Raman-active modes at 2 K in  $\text{Na}_2\text{O}_{60}$ . Parameters were determined by a single-component fitting.

Mode	$\text{Na}_2\text{C}_{60}$		
	$\omega_0$	$\Gamma$	$q$
Hg(1)	268	3	-11
	269	2	-42 <sup>a</sup>
	265	4	-15 <sup>a</sup>
Hg(2)	428	8	-3
Ag(1)	492	2	-1969
Hg(3)			
Hg(4)	769	4	-228
Ag(2)	1460	3	374

<sup>a</sup>Parameters determined by two-components fitting.

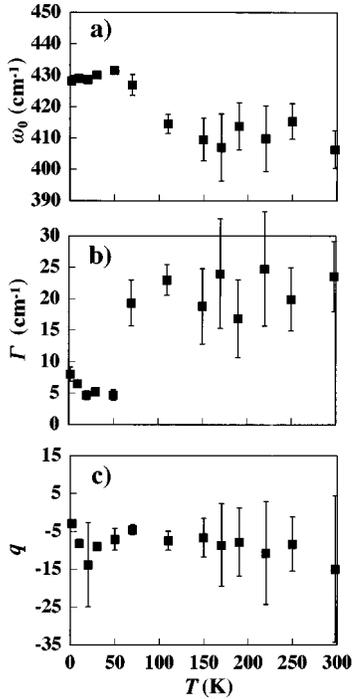


FIG. 7. Temperature dependence of (a) the  $\omega_0$ , (b)  $\Gamma$ , and (c)  $q$  for the Hg(2) mode.

rectly be compared with those in Ref. 35. The  $\omega_0$  observed in the temperature region from 50 to 2 K is consistent with those observed at room temperature for C<sub>60</sub> [430.5 cm<sup>-1</sup> at 300 K (Ref. 32)] and Rb<sub>6</sub>C<sub>60</sub> [428 cm<sup>-1</sup> at 298 K (Ref. 21)] which show the insulating behavior. The  $\Gamma$  showed a drastic decrease at 50 K; the  $\Gamma$  was approximately 20 cm<sup>-1</sup> above 50 K, while the  $\Gamma$  was approximately 5 cm<sup>-1</sup> in the temperature region from 50 to 2 K. The  $\Gamma$  at the higher temperatures than 50 K is close to that for Cs<sub>3</sub>C<sub>60</sub> at room temperature (16 cm<sup>-1</sup> at 290 K);<sup>21</sup> the  $\Gamma$  for the superconducting K<sub>3</sub>C<sub>60</sub> and Rb<sub>3</sub>C<sub>60</sub> were 75 and 74 cm<sup>-1</sup> at 300 K, respectively,<sup>32</sup> which were broader than that for the metallic but nonsuperconducting Cs<sub>3</sub>C<sub>60</sub>.<sup>21</sup> On the other hand, the  $\Gamma$  in the temperature region from 50 to 2 K is close to those for the insulating C<sub>60</sub> [5.5 cm<sup>-1</sup> at 300 K (Ref. 32)] and Rb<sub>6</sub>C<sub>60</sub> [4 cm<sup>-1</sup> at 298 K (Ref. 21)]. The temperature dependence of  $\Gamma$  indicates that the interaction between the electron and the intramolecular Hg(2) phonon in Na<sub>2</sub>C<sub>60</sub> in the temperature region from 50 to 2 K is remarkably different from that above 50 K. We confirmed from the temperature dependence of the  $\omega_0$  and  $\Gamma$  that Na<sub>2</sub>C<sub>60</sub> has the M-I transition at 50 K. The  $q$  was almost constant within the experimental error in all temperature region, and no drastic change was observed at 50 K. The reason why the  $q$  does not reflect the M-I transition at 50 K is not clear at the present stage. Recently, we observed almost the same  $q$  for the Hg(2) mode in the metallic Cs<sub>3</sub>C<sub>60</sub> and the insulating Rb<sub>6</sub>C<sub>60</sub>, in spite of the absence of the  $t_{1u}-t_{1u}^*$  transition for the insulating Rb<sub>6</sub>C<sub>60</sub>.<sup>21</sup> These facts reflect the difficulty in the estimation of  $q$  value for the Hg(2) peak.

## DISCUSSION

We examined some scenarios to account for the electronic state and the origin of the M-I transition in Na<sub>2</sub>C<sub>60</sub>. First, the

possibility of one or two-dimensional polymer was considered for Na<sub>2</sub>C<sub>60</sub>. If Na<sub>2</sub>C<sub>60</sub> took the polymer structure, a descent in symmetry of the C<sub>60</sub> molecule from  $I_h$  to a low symmetry such as  $D_{2h}$  should lead to the large splitting of each Raman-active mode. The large splittings were actually observed for all Hg modes and Ag(2) mode when RbC<sub>60</sub> transformed from the monomeric phase to the polymeric one.<sup>38,39</sup> Furthermore, we also observed the large splitting for the Hg(1), Hg(2), Hg(3), Hg(4), and Ag(1) peaks in the polycrystalline sample of polymeric RbC<sub>60</sub> at 298 K. However, such a large splitting was not observed for Na<sub>2</sub>C<sub>60</sub> in the temperature region from 298 to 2 K, though the small splitting was observed for the Hg(1) peak; the Hg(1) peak in the polymeric RbC<sub>60</sub> consisted of at least three components and the splitting was larger than that in Na<sub>2</sub>C<sub>60</sub>.<sup>40</sup> This fact suggests that Na<sub>2</sub>C<sub>60</sub> does not take a one-dimensional (1D) or two-dimensional (2D) polymeric structure in the temperature region. Consequently, it is difficult to attribute the M-I transition to the Peierls instability.

The second possibility was the Mott-Hubbard picture. The  $N$ -fold degenerate Hubbard model within the Gutzwiller approximation shows that the critical energy  $U_c$ , which separates an insulator from a correlated metal, sensitively depends on both the degeneracy and the electron-filling; the value of  $U_c$  is maximum at half filling ( $U_c/W=2.62$  for  $x=1$ , 3.65 for  $x=2$  and 4.00 for  $x=3$  in  $A_xC_{60}$  with  $N=3$ ).<sup>41</sup> Consequently, it is difficult for a degenerate system to become a Mott-Hubbard insulator near half filling, because the large electron-electron Coulomb repulsion  $U$  is required.<sup>41</sup> Thus,  $A_xC_{60}$  is expected to show a metallic behavior at  $x=3$  and an insulating or metal-insulator transition at  $x=2$  and 4.<sup>41</sup> If Na<sub>2</sub>C<sub>60</sub> has a slightly larger  $U/W$  than the  $U_c/W$ , it should be metallic above the critical temperature and insulating below the temperature. Such a scenario is presented for the high-temperature monomeric phase of Na<sub>4</sub>C<sub>60</sub>.<sup>7,13</sup> Only the monomeric Na<sub>4</sub>C<sub>60</sub> among  $A_xC_{60}$  with the bct structure was metallic because of the large  $W$  caused by the short interfullerene distance of 9.80 Å. This fact suggests that  $A_xC_{60}$  fullerides are the Mott-Hubbard insulators.<sup>7,13</sup> The  $W$  for the Na<sub>2</sub>C<sub>60</sub> is larger than that for the monomeric Na<sub>4</sub>C<sub>60</sub> judging from the  $\chi_{\text{spin}}$ . In spite of the larger  $W$ , Na<sub>2</sub>C<sub>60</sub> was insulating in the low-temperature region from 50 K. This fact suggests the Mott-Hubbard picture with a large  $U$  for Na<sub>2</sub>C<sub>60</sub>.

Furthermore, the Jahn-Teller distortion was considered as the origin of the M-I transition, because the conduction band in Na<sub>2</sub>C<sub>60</sub> is partially filled by an even number of electrons. The Hg(2) Raman peak for Na<sub>2</sub>C<sub>60</sub> showed the strong electron-phonon coupling above the M-I transition temperature and the drastic change with the M-I transition. The strong electron-phonon coupling may be an indication of the Jahn-Teller distortion in Na<sub>2</sub>C<sub>60</sub>. Taliani *et al.* pointed out that the occurrence of the asymmetric Fano line shape in the Hg(2) Raman mode was due to the splitting of  $t_{1u}$  conduction band that originates from the Jahn-Teller distortion or other interactions.<sup>35</sup> The small gap in the conduction band caused by the Jahn-Teller distortion can lead to the metallic behavior at high temperature and the insulating behavior at low temperature.

The temperature dependent x-ray diffraction did not give the experimental evidence for the Jahn-Teller distortion of

the  $C_{60}$  molecule in  $Na_2C_{60}$ , and showed no clear structural change at 50 K; the temperature dependence of the  $a$  and the Debye-Waller factor of Na atom from 2 to 280 K were well fitted by the Grüneisen relation and the Debye approximation, and the Rietveld analyses for the x-ray diffraction patterns at 10 and 50 K could be performed with the same space group and the same orientation of  $C_{60}$  of  $I_h$  symmetry as those at 298 K. Therefore, the M-I transition for  $Na_2C_{60}$  seems to be a transition without the structural change. However, if the Jahn-Teller distortion is dynamical, it is difficult to detect the structural distortion even at low temperature. Though the rapid decrease in the  $\chi_{spin}$  in the low-temperature region from 50 K supports the Mott-Hubbard transition, the decrease in the  $\Delta H_{pp}$  in the temperature region is not consistent with the Mott-Hubbard insulator, which should show an increase in  $\Delta H_{pp}$  because of the antiferromagnetic ground state. The behavior of the  $\chi_{spin}$  and the  $\Delta H_{pp}$  below the M-I transition seems to suggest the nonmagnetic ground state. If the M-I transition is attributed to the Jahn-Teller distortion, the ground state realized for the insulating  $Na_2C_{60}$  will be nonmagnetic.

In the present paper, it has been shown that the electronic

correlation and the Jahn-Teller effect should be considered to understand the origin of the M-I transition in  $Na_2C_{60}$ . The definitive evidence on the origin of the M-I transition will be given by the elucidation of the magnetic nature of the ground state below 50 K. When applying pressure to the insulating  $Rb_4C_{60}$ , this transformed to the metal under 8 kbar because of an increase in the  $W$  and the screening of the  $U$ .<sup>42</sup> This fact implies that the M-I transition disappears by applying pressure, if  $Na_2C_{60}$  is the Mott-Hubbard insulator as  $A_4C_{60}$ . Furthermore, the large electron-phonon coupling in  $Na_2C_{60}$ , which is comparable to that in  $Rb_3C_{60}$ , may lead to the superconducting transition at low temperature, when the M-I transition disappears under pressure.

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