Analysis of Ion Species in Potassium-Fullerene Plasmas

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Abstract
A detailed mass analysis using an “omegatron” analyzer is performed on ion species in magnetized potassium-fullerene plasmas produced by introducing “Buckminsterfullerene” particles into a low-temperature (≈ 0.2 eV) potassium plasma column. Negative fullerene ions are confirmed to be successfully produced by electron attachment. Mass spectra obtained yield negative ion components C_{60}^- and C_{70}^- with density ratio of C_{70}^- to C_{60}^- = 0.08 ~ 0.1, in addition to positive ion components ^{39}K^+ and ^{41}K^+ with density ratio of ^{41}K^+ to ^{39}K^+ = 0.06 ~ 0.08, being well consistent with constituent ratios of the fullerene- and potassium-particles supplied, respectively.

Keywords:
potassium-fullerene plasma, ion species, “omegatron” analyzer,

1. Introduction
Plasmas including dusts or fine particles are of current interest in various fields of physics and engineering such as astrophysics [1] and plasma-aided manufacturing [2]. These large particles are often negatively charged up in plasmas such that there is no net electric current to the particles. Even in case of ultrafine particles, if the electron affinity is large, they are negatively charged up in plasmas. From a viewpoint of understanding such dusty plasmas, particles with well-defined mass and size are often quite convenient. “Buckminsterfullerene” particles [3] are large cage-like molecules composed of many carbon atoms. Among various fullerenes, C_{60} particles are the most stable, having well-defined mass of mass number = 720 and size of about 0.7 nm in diameter. Since their electron affinity (≈ 2.65 eV) is large, the C_{60} particles become negative ions in low-temperature plasmas as a result of electron attachment, providing ultrafine-particle plasmas which include large negative ions in addition to positive ions and electrons. Such an ultrafine-particle plasma has been produced by introducing the fullerenes consisting mainly of C_{60} into a low-temperature (≈ 0.2 eV) potassium plasma column under a strong axial magnetic field [4]. Here we present a detailed mass analysis of ion species in the potassium-fullerene plasmas produced, which is performed by using an “omegatron” mass analyzer set at one end of the plasma column. The omegatron, the principle of which is based on ion cyclotron resonance, was originally used for residual gas analysis and for accurate mass determination [5]. Its application to plasma analysis has recently been developed in connection with investigating physics of plasma processing [6] and plasma-surface interaction [7].
2. Experimental Apparatus and Methods

The experiment is carried out in a single-ended Q machine [8] with a vacuum chamber, 15.7 cm in diameter and 400 cm length. A plasma consisting of electrons and potassium ions \( K^+ \) is produced by contact ionization of K atoms at a hot 5.2-cm-diam tungsten plate yielding a sufficient electron emission. The background gas pressure is \( P = (1 - 3) \times 10^{-4} \) Pa. The plasma, with density \( n_p = (1.0 \sim 5.0) \times 10^9 \) cm\(^{-3} \) and electron temperature \( T_e = 0.2 \) eV \( \geq T_+ \) (positive ion temperature), flows along a uniform magnetic field \( B = 2 \sim 4 \) kG. As shown in Fig. 1, the potassium plasma passes through a copper cylinder, 7.6 cm in diameter and 20 cm length, which has a heating system and is situated around the machine center. A 1.5-cm-diam and 2-cm-depth oven for sublimation of the fullerenes, which is made of copper and set in a 3-cm-diam hole on the side wall of the cylinder, has a small hole (0.2 \sim 0.4 cm in diameter) to inject the fullerenes. The temperature for \( C_{60} \) sublimation is in the range 350 \sim 400\(^\circ\)C. The oven temperature \( T_o \) is carefully changed to cover this temperature range (200 \sim 480\(^\circ\)C) while the cylinder temperature is kept around 400 \sim 450\(^\circ\)C.

Most of plasma parameters are measured by moveable Langmuir probes. The omegatron analyzer is situated behind a small hole of the metal endplate set at a distance of 210 cm from the hot tungsten plate, as shown in Fig. 1. The analyzer cell is cubical (10 cm \times 10 cm \times 10 cm), consisting of the following parts: (1) endplate, (2) front electrode with (8) orifice (about 0.15 cm in diameter), (3) top electrode, (4) bottom electrode grounded together with the hot plate and vacuum chamber, (5) back electrode, (6) collector grounded via a resistance and (7) two side electrodes. All of them are made of stainless-steel. The electrical circuit for measurements includes a function generator, four variable dc potential supplies for ion trapping and an X-Y recorder. The function generator supplies a radio frequency (RF) exciting signal which is applied to the top and bottom electrodes of the cubical box.

The principle of the omegatron is straightforward: When the frequency \( (\omega/2\pi) \) of the applied RF electric field is equal to the cyclotron frequency of one of the ion species passing through the orifice, the ion orbital radius increases until the ions arrive at the collector. Consequently, the curve of the collector current \( (I_c) \) against \( col_2/\omega \) yields a peak at this frequency. The trapping voltages of the electrodes are adjusted to give a maximum peak height at the fixed RF electric field. Their typical values are \( V_e = -4 \) V, \( V_f = 0 \) V, \( V_b = +1 \sim +3 \) V and \( V_* = 0 \sim -1.5 \) V in case of plasmas without appreciable fullerenes and \( V_e = \) floating potential \(+1 \) V, \( V_f = 0 \sim -2 \) V, \( V_b = -1.5 \sim -2 \) V and \( V_* = -2 \sim +3 \) V in case of the potassium-fullerene plasmas. Here \( V_e, V_f, V_b \) and \( V_* \) are the voltages applied to the endplate, front, back and side electrodes, respectively. The RF electric-field amplitude is \( 0.6 \sim 0.8 \) V/cm.

3. Experimental Results

The electron fraction \( 1 - \varepsilon \) in the potassium-fullerene plasmas is monitored by measuring a negative-saturation current \( (I_*) \) of the Langmuir probe, which depends on \( T_o \). Here \( \varepsilon = n_- / n_p \). \( n_0 = n_+ = n_e + n_- \) if \( Z = 1 \) with electron, positive and negative ion densities, \( n_e, n_+ \) and \( n_- \), respectively. Since the negative-ion production is due to the electron attachment to the fullerene particles, \( 1 - \varepsilon \) decreases with an increase in \( T_o \). Figure 2 shows a typical variation of \( I_* \) with \( T_o \) as a parameter, where the probe is set at the radial center just behind the copper cylinder. With an increase in \( T_o \), \( I_* \) is found to decrease, implying a decrease in \( n_e \) or an increase in the negative fullerene ions because there is no appreciable change in \( T_+ \). In this experiment, the electron fraction \( 1 - \varepsilon \) decreases down to the value around \( 1 \times 10^{-1} \) at the radial center. A plasma spread in the radial direction is observed in the presence of the negative fullerene ions with large Larmor radius.
At first, mass spectra (collector currents $I_c$ of the omegatron versus $\omega/2\pi$) are measured for positive ion species. They are almost independent of $T_0$. A typical example is inserted in Fig. 3, where $T_0 = 200^\circ$C and $B = 3.85$ kG. There is a large signal peaking around $\omega/2\pi = 150$ kHz in the spectrum. In addition to this sharp peak, a small peak is found a little below 150 kHz. The frequencies yielding these large (closed circles) and small (open circles) peaks ($\omega_{\text{peak}}/2\pi$) are plotted as a function of the magnetic field $B$ in Fig. 3.

![Fig. 2. Control of fullerene particles: negative probe-saturation current $I_s$ with oven temperature $T_0$ as a parameter.](image)

![Fig. 3. A typical example of mass spectra (inset): collector current $I_c$ (positive) of the "omegatron" against applied RF frequency $\omega/2\pi$ at $B = 3.85$ kG and $T_0 = 200^\circ$C. Frequencies at the large and small peaks in the spectrum as a function of magnetic field $B$. Solid lines indicate the predicted cyclotron frequencies of positive potassium ions $^{39}\text{K}^+$ and $^{41}\text{K}^+$.](image)
where two solid lines are given by the predicted ion cyclotron frequencies of K\(^+\) with mass numbers 39 and 41. It can be seen that the large and small peaks correspond to \(^{39}\)K\(^+\) and \(^{41}\)K\(^+\), respectively. By comparing these peak heights in the spectrum, the density ratio of \(^{41}\)K/\(^{39}\)K is estimated to be 0.06 - 0.08 which is around the value of the natural isotope abundance, 0.072.

When there are negative ions in plasmas, the collector of the omegatron yields negative signals in the mass spectra. The measured results of negative ion species are demonstrated with \(1 - \varepsilon\) as a parameter in Fig. 4, where \(B = 3.85 \text{ kG}\). It can be found that the mass spectra yield two peaks in the low-frequency range \(\lesssim 10 \text{ kHz}\), although one of them is quite small, in case of the potassium-fullerene plasmas \((1 - \varepsilon < 1)\). Both of the peak height increase with a decrease in \(1 - \varepsilon\) (i.e., an increase in the negative ion density), saturating for \(1 - \varepsilon \leq 0.3\). Figure 5 shows \(B\) dependences of the frequencies corresponding to the large (closed circles) and small (open circles) peaks in the mass spectra, where the predicted ion-cyclotron frequencies of \(C_{60}^-\) and \(C_{70}^-\) are indicated by solid lines. A good agreement is found between the measured and predicted values, showing that the large and small peaks are due to \(C_{60}^-\) and \(C_{70}^-\), respectively. From the

![Graphs showing collector current against applied RF frequency](image)

**Fig. 4.** Collector current \(I_c\) (negative) against applied RF frequency \(\omega/2\pi\) with electron fraction \(1 - \varepsilon\) as a parameter. \(B = 3.85 \text{ kG}\).

![Graphs showing frequencies at large and small peaks](image)

**Fig. 5.** Frequencies at the large and small peaks in Fig. 4 as a function of magnetic field \(B\). \(1 - \varepsilon = 0.5\). Solid lines indicate the predicted cyclotron frequencies of negative fullerene ions \(C_{60}^-\) and \(C_{70}^-\).
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4. Discussions and Summary

In our previous work [4], the existence of $C_{60}^-$ was proved by detecting ion-wave signals and $1 - \varepsilon$ was estimated from the measurements of ion-wave propagations in the potassium-fullerene plasmas. As presented above, we can now confirm $C_{70}^-$ in addition to $C_{60}^-$ and obtain the density ratio of $C_{70}^-$ to $C_{60}^-$ from the omegatron analysis. In our experiment, there often appear tiny peaks at frequencies lower than the cyclotron frequencies of $C_{60}^-$ and $C_{70}^-$ in the mass spectra, suggesting a generation of negative ions with heavier masses. However, they are often unstable and are observed only around $B = 4.0$ kG (almost the upper limit of our magnetic field). In order to confirm such massive negative ions, the omegatron mass-resolution has to be improved. For this purpose it is necessary to increase $B$ because the omegatron mass-resolution is proportional to $B^2$. It may also be promising to modify a geometrical configuration of the omegatron such as elongating RF electrodes along the magnetic field [7] or to employ RF fields traveling in the direction perpendicular to the magnetic field [9] instead of simply-oscillating RF fields.

In summary, measurements of ion species have been performed on magnetized potassium-fullerene plasmas. The omegatron mass analysis proves that negative fullerene ions are successfully produced by electron attachment in a low-temperature ($\approx 0.2$ eV) Q-machine plasma. We can conclude that there are negative ions $C_{60}^-$ and $C_{70}^-$, in addition to $^{39}K^+$ and $^{41}K^+$, in our potassium-fullerene plasmas. The density ratios of $C_{70}^-$ to $C_{60}^-$ and of $^{41}K^+$ to $^{39}K^+$ are negligibly small, being consistent with the constituents of the fullerene and potassium supplied in the experiment. This work provides an important base necessary for coming investigations to understand characteristic features of potassium-fullerene plasmas and/or to analyze potassium-fullerene thin films formed on the end-plate biased electrically.

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References