

整理番号	2020 - J - 092	報告者氏名	Prassides Kosmas
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研究課題名: カーボン材料を基盤とした高温超伝導体の創製: フラーレンへの内外双方向電子ドーピングによる電子構造の精密制御

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<研究内容・成果等の要約>

Superconductors have no electrical resistance and carry electricity without losing energy – finding new superconductors which work at high temperatures is important. The PI's landmark work established fullerides as the molecular systems with the highest superconducting transition temperature, T_c (38 K). He also found that superconductivity is not lost even under extremely high magnetic fields (up to 90 Tesla). Both record performances render C_{60} superconductors important technological materials. Achieving higher T_c to zero-resistance state is at the extreme forefront of current challenges and can transform existing and enable new technologies of tremendous economic and societal benefits in energy and healthcare. This was optimized for C_{60} superconductors in which externally-directed electron-doping of the molecular carbon framework was achieved by reaction with alkali metals. But further research has encountered a significant bottleneck: C_{60} lacks geometric and electronic versatility. Small changes of its molecular structure destroy its functionality and no other fullerene has shown superconductivity.

In this research, we investigate an innovative way to remove the roadblock by trying to use a new building block of the molecular superconducting architectures and develop a new mechanism to achieve control of the electronic and conducting properties. The new nanocarbon molecule is the endohedral metallofullerene $[Li@C_{60}]$, which incorporates a Li^+ ion encapsulated inside the C_{60} cage and exists as the neutral charge-balanced dimer, $(Li^+@C_{60}^{\bullet-})_2$. The new mechanism is dual-direction electron-doping of the nanocarbon framework, provided by the lithium metal inside the cage and by intercalated alkali metal ions outside the cage.

<研究発表（口頭、ポスター、誌上別）>

Journal Publication

- [1] R. H. Colman, H. E. Okur, G. Garbarino, Y. Ohishi, S. Aoyagi, H. Shinohara, K. Prassides, “*Pressure effects on the crystal structure of the cubic metallofullerene salt $[Li@C_{60}][PF_6]$ to 12 GPa*”, *Mater. Today Commun.* **2022**, *31*, 103272/1-7.

Conference Presentations

- [1] April 14, 2021
K. Prassides, “*Emergent electronic phenomena in all-carbon π -electron molecular systems*”, Joint Seminar Series of the Department of Condensed Matter Physics (DCMP) and the Materials Growth and Measurement Laboratory (MGML), Charles University, Prague, Czech Republic (**Online Invited Lecture**).
- [2] April 16, 2021
N. Yoshikane, K. Prassides, “*Valence tuning in rare-earth fullerides at ambient and elevated pressures*”, Inorganic Solid State Chemistry Division of the American Chemical Society, ACS Spring 2021 Meeting (**Online Lecture**).
- [3] May 20, 2021
K. Matsui, K. Prassides, “*Effect of chemical and physical pressure on rare-earth mixed valency in rare-earth fullerides*”, 37th Conference of the Rare-earth Society of Japan (**Online Lecture**).
- [4] August 3, 2021
K. Matsui, K. Prassides, “*Crystal structure of cation-ordered ternary fullerides M_2AC_{60}* ”, Summer School 2021, Young Coordination Chemists' Association of Japan (**Online Poster**).
- [5] August 4, 2021
N. Yoshikane, K. Prassides, “*Structural and electronic studies of rare-earth fullerides at elevated pressures*”, Summer School 2021, Young Coordination Chemists' Association of Japan (**Online Lecture**).
- [6] September 1, 2021
K. Matsui, K. Prassides, “*Systematic structural study of cation-ordered pentavalent fullerides*”, The 61st Fullerenes-Nanotubes-Graphene General Symposium (**Online Poster**).
- [7] September 20, 2021
N. Yoshikane, K. Prassides, “*Structural and electronic study of rare-earth fullerides by synchrotron XAS and XRD techniques at ambient and elevated pressures*”, 2021 Autumn Meeting, Condensed Matter Physics and Other Fields, The Physical Society of Japan (**Online Lecture**).
- [8] September 22, 2021
K. Matsui, K. Prassides, “*Synthesis and structural study of non-cubic cation-ordered ternary fullerides M_2AC_{60}* ”, 2021 Autumn Meeting, Condensed Matter Physics and Other Fields, The Physical Society of Japan (**Online Poster**).
- [9] December 6-8, 2021
K. Matsui, K. Prassides, “*Crystal Structure and Electronic Properties of Cation-Ordered Non-Cubic Pentavalent Fullerides*”, 2021 Fall Meeting, Materials Research Society (MRS) (**Online Lecture**).
- [10] December 6-8, 2021
N. Yoshikane, K. Prassides, “*Tuning of Mixed Valency in Rare-Earth Fullerides at Ambient and Elevated Pressures*”, 2021 Fall Meeting, Materials Research Society (MRS) (**Online Lecture**).

- [11] December 16-21, 2021
K. Prassides, “Mixed valency in alkali sesquioxides”, Symposium on “Electron transfer: from electrochemistry to mixed-valence molecules to photosynthesis”, PACIFICHEM 2021, The International Chemical Congress of Pacific Basin Societies (**Online Invited Lecture**).
- [12] December 16-21, 2021
K. Prassides, “Quantum magnetism in fully-frustrated all-carbon π -electron systems”, Symposium on “The Expanding Frontiers of Frustrated Magnetic Materials”, PACIFICHEM 2021, The International Chemical Congress of Pacific Basin Societies (**Online Invited Lecture**).
- [13] December 16-21, 2021
N. Yoshikane, K. Prassides, “Tuning rare-earth mixed valency by coupling to electronically-active fulleride anion sublattices”, PACIFICHEM 2021, The International Chemical Congress of Pacific Basin Societies (**Online Lecture**).
- [13] December 16-21, 2021
T. Fushimi, K. Prassides, “Spontaneous magnetoelastic effects in Prussian blue analogue molecular magnets”, PACIFICHEM 2021, The International Chemical Congress of Pacific Basin Societies (**Online Poster**).
- [14] May 27, 2022
K. Prassides, “Superconductivity and quantum magnetism in π -electron systems: a personal ongoing voyage into the unexpected”, Seminar Series of the Department of Chemistry, University of Crete, Greece (**Online Invited Lecture**).
- [15] June 23, 2022
K. Prassides, “Searching for the Hebel-Slichter coherence peak across the superconductivity dome of fullerides”, Superstripes 2022 International Conference, Frascati, Italy (**Online Invited Lecture**).
- [15] August 2-4, 2022
K. Matsui, K. Prassides, “Synthesis and structural study of pentavalent fullerides”, 2022 Summer School of the Young Coordination Chemists Association of Japan, Tokyo Institute of Technology (**Oral Lecture**).
- [16] August 2-4, 2022
M. Suzuki, K. Prassides, “Exploration of the Calcium- C_{60} Binary Phase Field”, 2022 Summer School of the Young Coordination Chemists Association of Japan, Tokyo Institute of Technology (**Poster Presentation**).
- [16] August 8-11, 2022
N. Yoshikane, K. Prassides, “Mixed valency in $(Sm_{1-x}Ca_x)_{2.75}C_{60}$ ”, 8th Asian Conference on Coordination Chemistry (ACC8C), Taipei, Taiwan (**Online Poster**).
- [17] August 8-11, 2022
M. Nishiura, K. Prassides, “Structural control of Prussian blue analogues by alkali metal substitution”, 8th Asian Conference on Coordination Chemistry (ACC8C), Taipei, Taiwan (**Online Poster**).
- [18] August 8-11, 2022
A. Matsumoto, K. Prassides, “Ab initio structural investigation of C_{60} /PAH co-adducts – new structures from powder diffraction data”, 8th Asian Conference on Coordination Chemistry (ACC8C), Taipei, Taiwan (**Online Poster**).
- [19] September 20-23, 2022
A. Tada, K. Prassides, “Valence-electron-count control of superconductivity in high-entropy alloys”, 2022 Autumn Annual Meeting, The Japan Institute of Metals and Materials, Fukuoka Institute of Technology (**Poster Presentation**).
- [20] September 26-28, 2022
N. Yoshikane, K. Prassides, “Mixed-valent rare-earth fullerides, $RE_{2.75}C_{60}$ ”, 72nd Japan Society of Coordination Chemistry Meeting, Kyushu University (**Oral Lecture**).
- [21] September 26-28, 2022
M. Suzuki, K. Prassides, “Novel Crystal Structure through Exploration of the Calcium- C_{60} ”

Binary Phase Field”, 72nd Japan Society of Coordination Chemistry Meeting, Kyushu University (**Poster Presentation**).

[22] September 26-28, 2022

M. Nishiura, K. Prassides, “Structural control of Prussian blue analogues by alkali metal substitution”, 72nd Japan Society of Coordination Chemistry Meeting, Kyushu University (**Poster Presentation**).

[23] September 26-28, 2022

A. Matsumoto, K. Prassides, “Ab initio structural investigation of C₆₀/PAH co-adducts – new structures from powder diffraction data”, 72nd Japan Society of Coordination Chemistry Meeting, Kyushu University (**Poster Presentation**).

[24] October 11, 2022

A. Tada, K. Prassides, “Design and fabrication of superconducting high-entropy alloys”, 8th Materials WEEK, The Society of Materials Science of Japan, Kyoto (**Poster Presentation**).

No. 3

<研究の目的、経過、結果、考察（5000字程度、中間報告は2000字程度）>

Compounds of C₆₀ have proved to be captivating materials, showing huge versatility and continued surprises. The accessible anionic charged states of C₆₀ has led to a wealth of research into the doping effects of alkali metals, alkaline earth metals and rare earths on the material's electronic properties, most notably for the observation of superconductivity in the A₃C₆₀ fullerides (where A = alkali metal). Understanding the pressure dependent structural properties of doped fullerides has been highlighted as a key issue since the discovery of superconductivity emerging from an antiferromagnetic Mott-insulating state under applied pressure in the highly expanded A₃C₆₀ fullerides. Cationically charged salts of C₆₀ have also been of interest as despite the poor electron donating abilities of C₆₀, hole doping is also expected to lead to interesting electronic properties. Experimental investigations of cationic fullerene salts are limited, even fewer examples have been isolated in the solid state. However, cationic functionalisation of fullerenes has recently resulted in the discovery of significant antimicrobial properties.

An alternative method for electronic doping of C₆₀, is to encapsulate the dopant within the C₆₀ cage. Endohedral encapsulation provides an important means of adjusting the physical properties of the material and a large number of fullerenes with endohedral encapsulation are now known, but a key problem in metallofullerene research is that of efficiently separating the endohedral fullerene from un-doped C₆₀. Using HPLC, several endohedral fullerenes have previously been isolated, with [Li@C₆₀]⁺ isolated in 100% encapsulation yield. The endohedral lithium fulleride was first purified and isolated as the antimony hexachloride salt [Li@C₆₀][SbCl₆] but it is the anion-exchanged salt [Li@C₆₀][PF₆] that has gained increased interest. Unlike the [SbCl₆]⁻ salt, [PF₆]⁻ crystallises in a rock-salt structure type, retaining the face-centred-cubic (fcc) lattice of metallofullerene subunits. The retention of a cubic packing structure is of particular interest when considering the possibilities of further doping with the aim of producing materials with interesting electronic properties.

Recently, Li@C₆₀ has been investigated as a multistate molecular switch, with up to 14 independent switched states and allowing for a huge increase in information density over binary

switch systems. Alternatively, an antiferroelectric ordering of the Li^+ ion, due to electrostatic interaction with the $[\text{PF}_6]^-$ counterion, < 24 K has been proposed as a possible qubit for quantum computing. Solutions of $[\text{Li}@\text{C}_{60}][\text{PF}_6]$ have also been shown to behave as excellent ionic conductors. Applying current to these solutions have then allowed electrochemical formation of the monovalent radical ion $\text{Li}^+@\text{C}_{60}^\bullet$. More recently an electrochemical reduction has led to the scalable and efficient synthesis of the monovalent radical ion $\text{Li}^+@\text{C}_{60}^\bullet$, which has been confirmed to dimerize in an analogous fashion to $(\text{C}_{59}\text{N})_2$.

Understanding the physical and electronic properties of these systems is key to realising future applications. The spectroscopic fingerprints of the $[\text{Li}@\text{C}_{60}][\text{PF}_6]$ salt have been investigated for identification of astrochemically produced endohedral fullerides. Encapsulation of cationic species that reside off-centre, such as $\text{Li}@\text{C}_{60}$, was found to activate additional vibrational modes, explained by a reduction of the species' symmetry with only minor modifications to the density-of-states from charge doping at room temperature. To further understanding of the $[\text{Li}@\text{C}_{60}][\text{PF}_6]$ system, this work addresses the compressibility of the $[\text{Li}@\text{C}_{60}][\text{PF}_6]$ salt. Investigating how the material reacts to external perturbations such as pressure is important for its potential in future applications and in designing new synthetic routes.

In an attempt to understand how the cubic crystal structure of the $[\text{Li}@\text{C}_{60}][\text{PF}_6]$ salts responds to changes in temperature and pressure, we have performed synchrotron X-ray powder diffraction measurements as a function of pressure to ~ 12 GPa at both ambient and cryogenic temperatures [1]. Under these conditions, the material adopts an orientationally ordered primitive cubic structure with no evidence of either a change in the orientational state of the $[\text{Li}^+@\text{C}_{60}]$ units or a transition to a low-symmetry fullerene-bridged polymer phase. The steric effects associated with the large $[\text{PF}_6]^-$ units, which reside in the octahedral interstices of the cubic close-packed arrangement of $[\text{Li}^+@\text{C}_{60}]$ endow the material with extreme structural robustness.

$[\text{Li}@\text{C}_{60}][\text{PF}_6]$ crystallises below 370 K with a primitive cubic structure (space group $P\bar{a}3$) based on face-centred packing of the $[\text{Li}^+@\text{C}_{60}]$ cages while the $[\text{PF}_6]^-$ units reside in the octahedral interstices. The endohedral cation, Li^+ , is dynamically-disordered inside the C_{60} cage at high temperatures but upon cooling below ~ 100 K, it localises onto one of two sites without any lowering of the crystal symmetry. Calculation of the nuclear wavefunctions along with energy decomposition analysis highlight the quantised motion of the Li^+ within the C_{60} confinement cage and clarify the origin of the localisation as an interplay between short-range exchange repulsion and long-range polarisation attraction. On further cooling below 24 K, synchrotron X-ray single crystal diffraction together with thermodynamic and dielectric measurements identified a subtle antiferroelectric ordering of the Li^+ ions, which now occupy a single preferred site, reducing the crystal symmetry to space group $P2_13$. However, this symmetry reduction affects neither the C_{60} cage nor the $[\text{PF}_6]^-$ anion and the weak $P2_13$ reflections, which break inversion symmetry are only due to the antiferroelectric order on a single Li^+ site.

Due to free rotation of the $[\text{Li}^+@\text{C}_{60}]$ cages, the high-temperature structure of $[\text{Li}@\text{C}_{60}][\text{PF}_6]$ ($T > 370$ K) is fcc (space group $Fm\bar{3}m$) isostructural to those of pristine C_{60} ($T > 260$ K) and some of its alkali salts such as CsC_{60} ($T > 350$ K) and $\text{Na}_2\text{CsC}_{60}$ ($T > 300$ K), in which alkali ions reside in the octahedral and tetrahedral interstices. On cooling into the low-temperature primitive cubic

structure, the $[\text{Li}^+\text{@C}_{60}]$ carbon cage in $[\text{Li}\text{@C}_{60}][\text{PF}_6]$ is found to occupy a single rotational orientation, which can be described as an anticlockwise rotation of $\phi \approx 101^\circ$ about the threefold [111] symmetry axis from that where the C-C double bonds would be aligned parallel to the axis directions. This contrasts sharply with the orientational disorder of the carbon cage in isostructural pristine C_{60} , (deeply quenched) CsC_{60} and $\text{Na}_2\text{CsC}_{60}$ in which two distinct rotational orientations are populated: a majority and a minority orientation at $\phi \approx 98^\circ$ and 38° , respectively. The population of these two orientations can be rationalised through local and global minima in the energy profiles resulting from interactions between neighbouring C_{60} cages.

The lack of orientational disorder in $[\text{Li}\text{@C}_{60}][\text{PF}_6]$ that contrasts with the properties of other known isostructural fullerene phases can be understood by comparing the size of the octahedral interstices to those of the ions which they accommodate. In pristine C_{60} , (deeply quenched) CsC_{60} and $\text{Na}_2\text{CsC}_{60}$, the octahedral holes are either vacant or occupied by Cs^+ ions whose size (1.70 Å) is smaller than that of the hole (2.06 Å). On the other hand, in $[\text{Li}\text{@C}_{60}][\text{PF}_6]$, the size of the $[\text{PF}_6]^-$ unit (2.54 Å) far exceeds that of the octahedral site presumably resulting in an increased rotational activation barrier, which precludes hopping of the carbon cages between orientations, which may be of comparable energy. A reduced entropy release at the rotational ordering transition in $[\text{Li}\text{@C}_{60}][\text{PF}_6]$ ($\Delta_{\text{trs}}S = 40.1(4) \text{ J K}^{-1} \text{ mol}^{-1}$), compared to pristine- C_{60} ($\Delta_{\text{trs}}S = 45.4(5) \text{ J K}^{-1} \text{ mol}^{-1}$), suggests that the rotational motion is restricted at temperatures even above the transition.

The observation that $[\text{Li}\text{@C}_{60}][\text{PF}_6]$ does not polymerise under hydrostatic pressure is not altogether surprising. Polymerisation is known in members of the AC_{60} series ($\text{A} = \text{K}^+, \text{Rb}^+, \text{Cs}^+$), where it occurs through [2+2] cycloaddition resulting in 1-dimensional chains. A different bonding mechanism through single C-C formation also leads to 1-dimensional polymerized fulleride chains in the $\text{Na}_2\text{AC}_{60}$ series but closest comparison may be made with pristine C_{60} due to the absence of charge on the carbon sphere in $[\text{Li}\text{@C}_{60}][\text{PF}_6]$. Pristine C_{60} is known to undergo dimerization under low hydrostatic pressure ($\sim 1\text{-}2 \text{ GPa}$) at ambient temperature as well as form numerous polymerised states of varying dimensionality when heated under pressure. The lack of dimer or polymer formation can be attributed to two key observations: the more expanded nature of the salt ($a/a(\text{C}_{60}) \sim 1.016$) due to the octahedral site occupation by the large $[\text{PF}_6]^-$ ion leads to increased intermolecular C-C contact distances; and the lack of $[\text{Li}^+\text{@C}_{60}]$ free rotational motion at both ambient temperature and 7 K. The increased steric effects of the $[\text{PF}_6]^-$ unit presumably hinder the large-amplitude librational motions required to orient the $[\text{Li}^+\text{@C}_{60}]$ units in a configuration conducive to intermolecular C-C bond formation.

In this study, we have used synchrotron X-ray radiation in combination with a diamond anvil cell to study how the structure responds to pressure at both ambient and low temperatures [1]. Unlike pristine C_{60} , the system shows a single orientation of the carbon cages due to unfavourable steric interactions between the interstitial $[\text{PF}_6]$ unit and C_{60} when rotated to effects of the $[\text{PF}_6]$

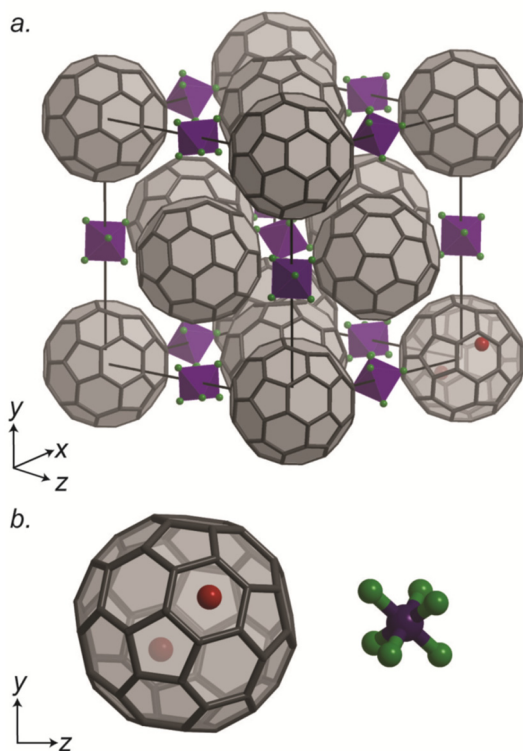


Figure 1. (a) The primitive cubic crystal structure of $[\text{Li}@\text{C}_{60}][\text{PF}_6]$. The $[\text{PF}_6]^-$ ions reside in the octahedral interstices. The endohedral Li^+ ions are shown inside only one C_{60} unit for clarity. (b) The endohedral Li^+ ions are disordered over two symmetry-equivalent sites within each C_{60} cage. Phosphorus, fluorine and lithium atoms are depicted as violet, green and red spheres, respectively.

unit, limiting librational motion to any other expected orientation (Figure 1). The expanded nature of the salt as well as the steric motion, prevent polymerisation through intermolecular C-C bond formation and no other signs of symmetry breaking or significant structural change were observed across the pressure and temperature range studied. The extracted bulk modulus is typical of a face-centred-cubic fulleride, confirming the non-interacting nature of both the $[\text{PF}_6]$ unit and the endohedral Li^+ ion (Figure 2).

In conclusion, we have performed a comprehensive compressibility study of the metallofullerene salt, $[\text{Li}@\text{C}_{60}][\text{PF}_6]$ at both ambient and low temperatures using synchrotron X-ray powder diffraction. The orientationally ordered primitive-cubic structure of $[\text{Li}@\text{C}_{60}][\text{PF}_6]$ survives with no signs of symmetry breaking or significant structural changes across the temperature and pressure range investigated in this work. In contrast to orientationally disordered primitive-cubic pristine C_{60} and some of its salts ($\text{Na}_2\text{AC}_{60}$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$), deeply quenched CsC_{60}), the system is orientationally ordered adopting only a single orientation of the carbon cages (anticlockwise rotation of $\sim 101^\circ$ about the $[111]$ cube diagonal) due to unfavourable steric interactions between the large interstitial $[\text{PF}_6]^-$ unit and $[\text{Li}^+@\text{C}_{60}]$ at other orientations. The expanded nature of the salt as well as the steric effects of the $[\text{PF}_6]^-$ unit, severely limiting rotational motion, also prevent polymerisation through C-C bond formation between fullerene units, again in sharp contrast to pristine C_{60} and its primitive cubic salts. The extracted bulk moduli, K_0 at both ambient and low temperatures are typical of those of a cubic-close-packed fullerene-based solid, consistent with the absence of interaction between the $[\text{PF}_6]^-$ unit and the endohedral Li^+ ion.

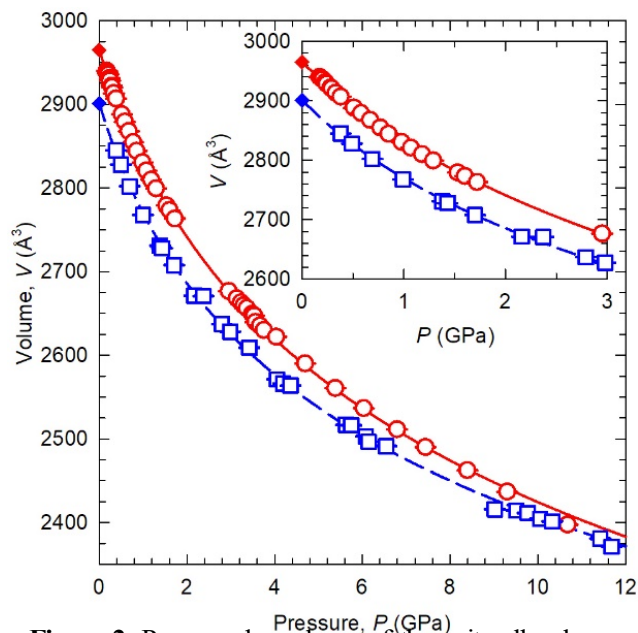


Figure 2. Pressure dependence of the unit cell volume of $[\text{Li}@\text{C}_{60}][\text{PF}_6]$ at 7 K (blue squares) and at ambient temperature (red circles). Lines through the data points represent least-squares fits to the second-order Murnaghan equation. Diamond symbols mark the corresponding unit cell volumes at ambient pressure. The inset shows an expanded view of the diagram at low pressures.

Reference

[1] R. H. Colman, H. E. Okur, G. Garbarino, Y. Ohishi, S. Aoyagi, H. Shinohara, K. Prassides, *Mater. Today Commun.* **2022**, *31*, 103272.