Superconductivity in Li$_3$Ca$_2$C$_6$ intercalated graphite

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In this letter, we report the discovery of superconductivity in Li$_3$Ca$_2$C$_6$. Several graphite intercalation compounds (GICs) with electron donors, are well known as superconductors$^1$. It is probably not astonishing, since it is generally admitted that low dimensionality promotes high superconducting transition temperatures. Superconductivity is lacking in pristine graphite, but after charging the graphene planes by intercalation, its electronic properties change considerably and superconducting behaviour can appear. Li$_3$Ca$_2$C$_6$ is a ternary GIC$^2$, for which the intercalated sheets are very thick and poly-layered (five lithium layers and two calcium ones). It contains a great amount of metal (five metallic atoms for six carbon ones). Its critical temperature of 11.15 K is very close to that of CaC$_6$ GIC$^{3,4}$ (11.5 K). Both CaC$_6$ and Li$_3$Ca$_2$C$_6$ GICs possess currently the highest transition temperatures among all the GICs.

Since forty years, we know that KC$_8$ GIC becomes superconductor$^5$ at very low temperature (0.14 K$^6$). More recently, metastable binary compounds obtained by high-pressure methods show higher critical temperatures: 1.9 K for LiC$_2$, 3 K for KC$_3$, 5 K for NaC$_2$ or 5.5 K for KC$_4$.$^8$ On the other hand, ternary GICs prove to be superconductors as KHgC$_8$ (1.90 K)$^9$, KTI$_{1.5}$C$_4$ (2.70 K)$^{10}$ or CsBi$_{0.5}$C$_4$ (4.05 K)$^{11}$. But, very recently, two binary GICs have been shown to become superconductors at higher temperatures: YbC$_6$ exhibits a critical temperature, T$_c$, of 6.5 K$^3$, and in CaC$_6$, T$_c$ reaches 11.5 K$^{3,4}$.

Our recent works concerning the intercalation into graphite of lithium-calcium alloys$^2$ showed the existence of two ternary lithium-calcium GICs belonging to the first stage, denoted $\alpha$ and $\beta$. This method can be used also in order to synthesise$^{12}$ bulk CaC$_6$. In this binary, only one calcium plane is intercalated between two successive graphene layers. On the contrary, both $\alpha$ and $\beta$ ternary GICs possess intercalated alloy sheets consisting of several atomic layers. Indeed, five layers are present in an intercalated sheet of $\alpha$ compound, according to the Li-Ca-Li-Ca-Li stacking and seven layers in a $\beta$ compound sheet, with the Li-Ca-Li-Li-Ca-Li sequence. Their repeat distances are 776 and 970 pm for $\alpha$ and $\beta$ compounds respectively, instead of 335 pm in pristine graphite. The chemical formulas reveal differences of intercalated metal amounts: Li$_{0.5}$Ca$_3$C$_6$ for $\alpha$ phase, and Li$_3$Ca$_2$C$_6$ for $\beta$ one. These formulas were obtained from data collected by nuclear microprobe techniques$^{13}$.

As reported in the following, only the $\beta$ phase exhibits a superconducting behaviour. Consequently, we will give some structural details$^2$ about the $\beta$ compound only. Since the e-
axes of all the crystallites forming the HOPG platelet are parallel to each other, the Li₃Ca₂C₆ sample c-axis direction is well-defined. The resulting 00l X-ray reflections are isolated (Fig. 1a). All of them can be identified as 00l ternary β compound reflections, confirming the sample high purity.

By Fourier transform of the 00l structure factors, the c-axis electronic density profile of the compound was shown in Fig. 1b and compared to the calculated one from an atomic stacking model. Of course, we searched to fit at best both profiles, taking chemical formula into account. Thus, the seven atomic layers present in the Li₃Ca₂C₆ intercalated sheet appear clearly. The three central lithium layers are flanked by two calcium ones and in turn by two more lithium layers.

While the sample c-axis is well-defined, the crystallites forming HOPG platelets are disordered in perpendicular directions, leading to an average of a and b directions, denoted as ab. The Li₃Ca₂C₆ hk0 reflection study exhibits an hexagonal 2D unit cell, commensurate with that of graphite, and an « a » parameter of 745 pm, three times larger than the graphitic one. Nevertheless, the atomic positions inside the cell are difficult to specify, so that the Li₃Ca₂C₆ space group is currently unknown.

Superconductivity does not appear for α compound above 2 K, while it is revealed at 11.15 K for β one. Fig. 2 shows the results concerning β compound for both ZFC and FC measurements. We observed a clear diamagnetic transition at 11.15 K under an applied field of 50 Oe. However, the saturation of diamagnetism is not reached down to 2 K.

The critical fields and the superconducting volume fraction were estimated from magnetization measurements versus applied field M(H) at several temperatures. Thanks to the 2D character of GICs, two directions were studied : - applied field parallel to c-axis (//c) or – perpendicular to c-axis (∥ab). For these data, we have taken into account the demagnetization correction due to sample shapes. In this case, the field is corrected with the following relation 

\[ H = H_0 - 4\pi NM \] (CGS units), where \( H_0 \) is the applied field, \( N \) is the shape correction factor and \( M \) is the magnetization of the sample. For the applied field parallel to c-axis, the N factor has been estimated to 0.7-0.8, and for the applied field perpendicular to the c-axis, the correction is negligible. As usual, the penetration length of the magnetic field in the sample was supposed quite weak so that we have disregarded the corresponding correction.

The superconducting volume fraction, calculated from the M(H) measurements with H applied parallel to the c-axis, was evaluated at 55 ± 5 %.
The magnetic phase diagram for the $\beta$ phase is presented in Fig. 3. This material appears as a type II superconductor. Indeed, the lower critical field $H_{c1}$, defined as the linearity break in the first part of the $M(H)$ curve at a given temperature, is approximately the same for both geometries (with extrapolated values: $H_{c1/ab}(0) = 32$ Oe and $H_{c1/c}(0) = 30$ Oe). However, the upper critical field, $H_{c2}$, defined as the beginning of the second linear domain, exhibits a sizable anisotropy: we estimate zero temperature extrapolated values $H_{c2/ab}(0)$ and $H_{c2/c}(0)$ of about 3100 Oe and 2000 Oe respectively, leading to a ratio $(H_{c2/ab} / H_{c2/c})$ closed to 1.5. A so small anisotropic ratio implies that superconducting state of this material is anisotropic but three dimensional in spite of its layered structure, as already noticed in YbC$_6^3$ and CaC$_6^4$ compounds.

Although the measurements were repeated, using several « crystallographic pure samples », the complexity of Li$_3$Ca$_2$C$_6$ structural building probably generates defects which not allow to reach the complete diamagnetic saturation. However, Li$_3$Ca$_2$C$_6$ unambiguously appears as a new superconductor below 11.15 K. Currently, this compound possesses the highest critical temperature among the ternary GICs.

**Methods**

We have shown that the ternary GICs containing lithium are extremely unusual and very difficult to synthesise$^{14}$. Indeed, various lithium-calcium ternary GICs were prepared using a well established protocol consisting of several successive steps$^{15}$.

For the $\beta$ compound, it is necessary, in a first time, to synthesise a lithium-calcium alloy, whose composition is Ca$_{0.25}$Li$_{0.75}$. It is obtained with extremely pure lithium and calcium reagents, which are molten and well-homogeneously mixed, using a furnace in a glove box containing a very pure argon atmosphere. In a second time, a highly oriented pyrolytic graphite (HOPG) platelet is introduced in the liquid alloy, using a tungsten sample holder, in order to maintain an excellent contact between graphite and alloy. The intercalation reaction is carried out during 10 days at 250°C for one sample and at 300 °C for the second sample in a stainless steel reactor under pure argon atmosphere (this temperature range needs to be strictly observed, because, if the reaction temperature increases until 350°C, the reaction product becomes pure CaC$_6$ instead of the pure $\beta$ ternary GIC). In a third time, when the reaction is ended, the bulk sample is carefully extracted of the liquid alloy. Then a two-sided cleavage of the intercalated platelet is performed in order to avoid any alloy deposit and surface defects. Finally, the sample is packed for its subsequent study.
The intercalated sample exhibits a pale yellow colour and the characteristic metallic brightness, with a remarkably strong hardness. By X-ray diffraction, it is very easy to isolate the 00l reflections of the sample in order to test its purity.

Magnetization of the $\alpha$ and $\beta$ compounds is measured as a function of temperature and magnetic field, using a Quantum Design MPMS5 SQUID magnetometer. Because of their reactivity, the samples have to be kept in a closed silica cell, under helium atmosphere. The samples are cooled down to 2 K without applied magnetic field. A field of 50 Oe is then applied and the magnetization of the samples is measured between 2 K and 15 K by steps of 0.2 K (« zero field cooling » experiment (ZFC)). After, the samples are cooled down to 2 K under the same field used in ZFC measurements. Then magnetization measurements (« field cooling » experiment (FC)) are performed like previously.

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Fig. 1: a) 00l X-ray diffraction pattern for Li$_3$Ca$_2$C$_6$ (Mo K$_{\alpha1}$), b) experimental and calculated c-axis electronic density profiles for Li$_3$Ca$_2$C$_6$. 
Fig. 2: Magnetization of $\text{Li}_3\text{Ca}_2\text{C}_6$ versus temperature with a 50 Oe field applied parallel to the $\text{c}$-axis (field cooling FC, and zero field cooling ZFC measurements).
Fig. 3: Superconducting phase diagram for Li$_3$Ca$_2$C$_6$ compiled from M(H) measurements at given temperatures. M(H) data were collected with the external field applied parallel to the c-axis (H$_{c1//c}$, H$_{c2//c}$) and in the perpendicular plane (H$_{c1//ab}$, H$_{c2//ab}$).