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Journal of Solid State Chemistry 179 (2006) 1289–1292

JOURNAL OF SOLID STATE CHEMISTRY

www.elsevier.com/locate/jssc

Rapid Communication

Superconductivity in $Li_3Ca_2C_6$ intercalated graphite

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Received 14 December 2005; received in revised form 17 January 2006; accepted 28 January 2006

Abstract

In this paper, we report the discovery of superconductivity in $Li_3Ca_2C_6$. Several graphite intercalation compounds (GICs) with electron donors, are well known as superconductors [T. Enoki, S. Masatsugu, E. Morinobu, Graphite Intercalation Compounds and Applications, Oxford University Press, Oxford, 2003]. 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. $Li_3Ca_2C_6$ is a ternary GIC [S. Pruvost, C. Hérold, A. Hérold, P. Lagrange, Eur. J. Inorg. Chem. 8 (2004) 1661–1667], 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 [T.E. Weller, M. Ellerby, S.S. Saxena, R.P. Smith, N.T. Skipper, Nat. Phys. 1 (2005) 39–41; N. Emery, C. Hérold, M. d'Astuto, V. Garcia, Ch. Bellin, J.F. Marêché, P. Lagrange, G. Loupias, Phys. Rev. Lett. 95 (2005) 087003] (11.5 K). Both CaC_6 and $Li_3Ca_2C_6$ GICs possess currently the highest transition temperatures among all the GICs.

Keywords: Graphite; Intercalation; Lithium; Calcium; Superconductivity; Magnetisation

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1. Introduction

Since 40 years, we know that KC_8 graphite intercalation compound (GIC) becomes superconductor [1] at very low temperature (0.14 K [2]). 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 [3] or 5.5 K for KC_4 [4]. On the other hand, ternary GICs prove to be superconductors as $KHgC_8$ (1.90 K) [5], $KTl_{1.5}C_4$ (2.70 K) [6] or $CsBi_{0.5}C_4$ (4.05 K) [7]. 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 [8], and in CaC_6, T_c reaches 11.5 K [8,9].

Our recent works concerning the intercalation into graphite of lithium–calcium alloys [10] showed the existence of two ternary lithium–calcium GICs belonging to the first stage, denoted α and β. This method can be used also in order to synthesise [11] bulk CaC_6. In this binary, only one calcium plane is intercalated between two successive graphene layers. On the contrary, both α and β ternary GICs possess intercalated alloy sheets consisting of several atomic layers. Indeed, five layers are present in an intercalated sheet of α compound, according to the Li–Ca–Li–Ca–Li stacking and seven layers in a β compound sheet, with the Li–Ca–Li–Li–Li–Ca–Li sequence. Their repeat distances are 776 and 970 pm for α and β compounds, respectively, instead of 335 pm in

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0022-4596/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2006.01.053

pristine graphite. The chemical formulas reveal differences of intercalated metal amounts: $Li_{0.5}Ca_3C_6$ for α phase, and $Li_3Ca_2C_6$ for β one. These formulas were obtained from data collected by nuclear microprobe techniques [12].

2. Experimental

We have shown that the ternary GICs containing lithium are extremely unusual and very difficult to synthesise [13]. Indeed, various lithium–calcium ternary GICs were prepared using a well-established protocol consisting of several successive steps [14].

In order to prepare the β 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 (from Aldrich, 99.9%, and then purified) and calcium (Aldrich, 99.99%) 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 (Carbone Lorraine) 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 (10 mm in diameter, 80 mm in height) 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 β 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, because it is sensitive to air.

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 $0\,0\,l$ reflections of the sample in order to test its purity.

Magnetisation of the α and β compounds is measured as a function of temperature and magnetic field, using a Quantum Design MPMS5 SQUID magnetometer. Because of their reactivity and to insure a good thermal exchange, 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 magnetisation of the samples is measured between 2 and 15 K by steps of 0.2 K ("zero field cooling (ZFC)" experiment). After, the samples are cooled down to 2 K under the same field used in ZFC measurements. Then magnetisation measurements ("field cooling (FC)" experiment) are performed like previously.

3. Results and discussion

As reported in the following, only the β phase exhibits a superconducting behaviour. Consequently, we will give some structural details [10] about the β compound only. Since the *c*-axis of all the crystallites forming the HOPG platelet are parallel to each other, the $Li_3Ca_2C_6$ sample *c*-axis direction is well-defined. The resulting $0\,0\,l$ X-ray reflections are isolated (Fig. 1a). All of them can be identified as $0\,0\,l$ ternary β compound reflections, confirming the sample high purity.

By Fourier transform of the $0\,0\,l$ structure factors (8 reflections), 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 $Li_3Ca_2C_6$ 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 $Li_3Ca_2C_6$ $h\,k\,0$ 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 $Li_3Ca_2C_6$ space group is currently unknown.

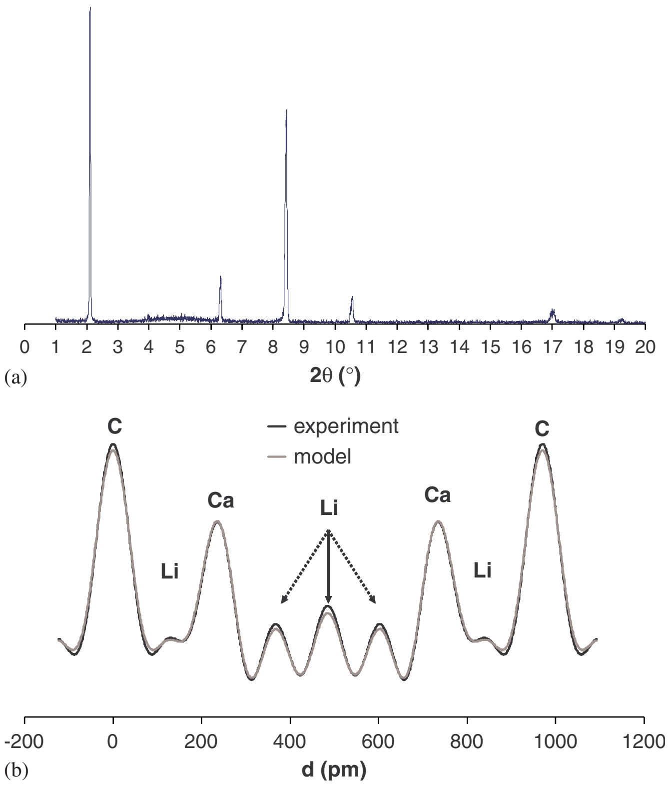

Fig. 1. (a) $0\,0\,l$ X-ray diffraction pattern for $Li_3Ca_2C_6$ (Mo$K\alpha1$), (b) experimental and calculated *c*-axis electronic density profiles for $Li_3Ca_2C_6$.