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Researching face centered cubic Cs_3C_{60}

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The possible formation of a fcc Cs_3C_{60} phase which should have a high critical temperature is critically reviewed. Temptative synthesis of this derivative has been realized by playing on the kind of defects present in solid C_{60} and also by reacting C_{60} either with cesium vapor or with cesium dissolved in liquid ammonia. Whatever the experimental conditions, the fcc phase was never formed. Moreover, we could not observe the formation of bcc Cs_3C_{60}. Opposite to many statments, temperature does not modify drastically the nature of the phases formed, and even heat treatment up to 750°C leads, after cooling down, to a mixture of A15 and bct phases, whatever the method of preparation.

Keywords: fullerenes, cesium, intercalation, structure, phase transitions, superconductivity

INTRODUCTION

Since the discovery of superconductivity in the face centered cubic K_3C_{60} phase [1,2], there were many trials for increasing the critical temperature of alkali doped fcc phases. From the observations of Fleming et al. showing that T_c increases monotonically with the size of the fcc cell [3], it appeared very quickly that the diameter of the intercalated species plays an important role. This was clearly demonstrated by the intercalation of ammonia in Na_2CsC_{60} (T_c = 10.5K; a = 14.13Å) which produces the compound $(NH_3)_4Na_2CsC_{60}$

(T_c = 10.5K; a = 14.13Å) which produces the compound $(NH_3)_4Na_2CsC_{60}$ with an expanded unit cell (a = 14.47Å) and an increased T_c of 29.6K [4]. However, superconductive properties can also easily disappear by small distortion of the fcc cell, as it happens when ammonia reacts with K_3C_{60} [5].

The highest T_c reached until now with the alkali doped phases at ambient pressure is 33K for Cs_2RbC_{60} [6]. Due to the important diameter of cesium, one can predict that a fcc Cs_3C_{60} phase should have the highest T_c in the series of alkali metal derivatives of C_{60}. Actually, the estimate made from band structure calculations for a hypothetical fcc cell gives T_c=47.4K [7]. On the other hand, calculations of heat of formation using an ionic model associated with a Born Haber cycle showed that fcc Cs_3C_{60} should be stable [8]

The first attempt to prepare a cesium-doped superconductive phase has proved unsuccessful [9]. Later a reproducible superconducting transition has been observed at 30K in Cs_xC_{60} prepared by using as the dopant binary alloys of the type CsM (M = Hg, Tl or Bi) [10]. However composition and structure of these compounds have not been determined. It cannot be excluded that ternary intercalation complexes ($Cs_xM_yC_{60}$) have been formed, as it is the case for the same reaction with graphite [11]. Such ternary phases with graphite have a superconducting behavior [12]. By allowing to react the C_{60}/C_{70} extract with a stoichiometric amount of cesium vapor at 220°C, we were able to prepare a Cs_3C_{60} compound. Its diffractogram was indexed on the basis of a body-centered cubic cell with a = 11.82Å [13]. This sample presented a superconductive transition at about 30K which disappeared after annealing at 380°C [14]. Occurrence of superconductivity at 29K in Cs_3C_{60} was confirmed by Kinoshita [15]. However, the superconducting volume fraction is roughly one order of magnitude smaller than for the parent potassium or rubidium derivatives. Further annealing at 408°C led to depress the fraction of superconductive material, showing that the hypothetic phase which could be responsible for superconductivity is decomposed by the effect of temperature.

In fact it was reported several times that a compound with the nominal composition Cs_3C_{60} is metastable and that Cs_1C_{60} and Cs_4C_{60} are readily synthesized and are the energetically more stable phases [16,17]. Keeping this observation in mind, it was then proposed to synthesize Cs_3C_{60} by the reaction of C_{60} with cesium dissolved in liquid ammonia [18]. The A_g Raman mode appearing at 1447 cm^{-1} after doping is the signature of three electrons transfered, and it also demonstrates the stability of a Cs_3C_{60} phase at low temperature. On further annealing the sample at 200°C, the A_g mode splits into two broad lines as the proof of phase separation of Cs_3C_{60} at elevated temperature into Cs_1C_{60} and Cs_4C_{60}. The X ray pattern of the low

temperature sample cannot be indexed in a fcc cell but rather as a two-phase mixture of cubic A15 and body-centered tetragonal (bct) structures. Upon applying hydrostatic pressure, superconductivity was observed at 40K. At 26kbar, the X ray pattern is comparable to the one which we obtained from the vapor phase reaction at ambient pressure [13]. It can be described by a single bcc structure with a=11.52Å against 11.82Å for our compound. So far, it appears that a bcc cell would be responsible for superconductivity in the case of Cs_3C_{60}.

The size mismatch between the radius of the tetrahedral sites (r_{tetra}=1.15 Å) in the C_{60} fullerite and the ionic radius of Cs (1.69 Å) could explain the unstability of fcc Cs_3C_{60} or at least the difficulty to form this phase. Even if temperature is a parameter which could affect the stability of fcc Cs_3C_{60}, it appears from all the attempts that other parameters could play an important role as for example non stoichiometry or the presence of impurities or defects. Expecting that stacking faults identified in solid C_{60} prepared by rapid precipitation (ABAB hexagonal stacking in the ABCABC cubic stacking) [19] could favor the intercalation of cesium in the tetraedral cavities and the formation of a fcc structure, samples were synthesized with the Cs/C_{60} ratio equal to 3 and using C_{60} free or not free of defects. Syntheses were realized either by direct reaction with cesium vapor or at low temperature in liquid ammonia. In order to better determine the influence of temperature on the nature of the phases existing in a sample with nominal composition Cs_3C_{60}, we carried out "in situ" X-ray diffraction in the range [25°C-800°C].

EXPERIMENTAL

For our study, we used two kinds of solid C_{60}: samples qualified as normal from different origins (Mer, Hoechst, Technocarbo) and an other one with stacking defects, prepared by Technocarbo, Grasse, France, through rapid precipitation in acetone [19].

For the vapor phase reaction, stoichiometric amounts of C_{60} (0.3g) and metallic Cs (Cs/C_{60}=3) were mixed in a Pyrex tube. C_{60} was outgassed at 200°C under residual pressure of 10^{-5} mbar and cesium was distillated. The tube was then sealed and the mixture was annealed at 225°C for 3 days. For the reaction in liquid ammonia, solid C_{60} (0.4g) was dipped in a Cs-NH_3 blue solution (Cs/C_{60}=3) at 194K (solid CO_2-ethanol bath). In the course of the reaction the blue color of the solution was disappeared and the product was dissolved. After a few hours, a solid was precipitated and ammonia excess was evaporated by slowly increasing temperature to 20°C. Measurement of ammonia pressure in a calibrated volume before and after the reaction

enabled to determine that the composition of the sample at this step is almost $Cs_3(NH_3)_5C_{60}$. Ammonia was further totally removed from the reaction product, first by cryopumping at room temperature and then under vacuum (10^{-5} mbar) at 150°C during 20 hours.

The samples were transferred in a glove box into quartz capillaries and Pyrex tubes respectively for X ray and NMR experiments. Powder X ray diffraction patterns were recorded at λ=0.70926 Å with a Curve Position Sensitive Detector (INEL CPS 120). "In situ" experiments were performed in the temperature range [25°C-750°C] using a furnace allowing to work in the transmission mode on quartz capillaries [20]. ^{13}C NMR measurements have been carried out at room temperature on a broad-band Bruker DSX spectrometer working at 8.5 Teslas (^{13}C resonance at 90 MHz). We have used a simple one-pulse technique, with phase cycling and signal averaging on several scans.

RESULTS AND DISCUSSION

Samples prepared from ammonia solution

Whatever the origin of C_{60}, containing defects or not, the samples prepared from ammonia solution are a mixture of A15 (a=11.8 Å) and bct (a=b=12.38 Å, c=11.4 Å) phases, comparable to that published by Palstra et al [18] (Fig. 1a), however with a lower contribution of the A15 phase in our case. Defects in pristine C_{60} are not responsible for the nature of the phases obtained, since in the two cases the solids are formed by precipitation from a solution. Heating the compound does not affect noticeably the relative proportions of the two phases up to 650°C. Above this temperature the lines relative to the A15 structure begin to disappear with a simultaneous increase of background (Fig. 1b). This is a little bit in contradiction with the interpretation that the Raman splitting observed at 200°C is due to a phase separation into Cs_1C_{60} and Cs_4C_{60} [18]. At 750°C the diffractogram consisted of a large background characteristic of the molten A15 phase, together with the lines belonging to the remaining bct phase (Fig. 1c). After rapid cooling from 750°C to 25°C the A15 phase reappeared only slightly diminished, indicating that its melting is almost a reversible transition (Fig. 1d). This difference in behavior between the two phases is consistent with electrostatic calculations of the cohesive energy due to ionic bonds in the Rb-C_{60} system showing that a bct (A_4C_{60}) structure is more stable (0.1 eV) than the A15 structure (A_3C_{60}) (0.2 eV) [21]. However, Rietvelt refinement for the bct phase formed with the initial ratio selected here, i.e. Cs/C_{60} = 3, indicates a composition close to Cs_3C_{60} [18].

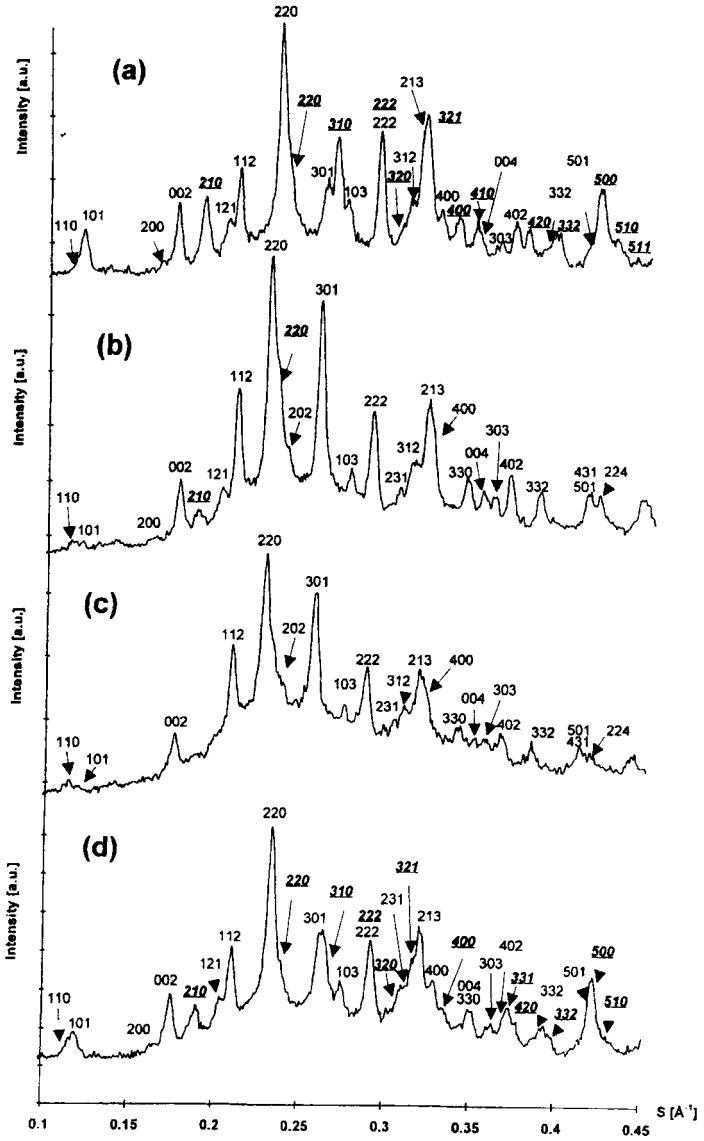

Figure 1: Diffractograms of Cs_3C_{60} prepared from ammonia solution; (a) room temperature; (b) 650°C; (c) 750°C; (d) room temperature after the thermal treatment. The lines with normal style indexes are attributed to Cs_4C_{60} (a=12.38 Å, c=11.4 Å); the bold and underlined indexes correspond to the A15 structure (a=11.8 Å).

As for X ray diffraction, the NMR experiments on the doped samples resulting of outgassing at 150°C gave the same results for the two kinds of C_{60} specimens. The ^{13}C NMR spectra present three lines at +178, +180, and +199 ppm (Table 1), respectively attributed to fcc Cs_1C_{60} [22-24], bct Cs_4C_{60} [25], and A15 Cs_3C_{60} [26]. The T_1 values were got as only rough estimates from the evolution of the line intensities *vs* recycling time. Using longer recycling times, we could not detect any evidence of signals with longer T_1 values, which should arise from phases like Cs_6C_{60} or undoped C_{60}. Compared to X ray diffraction, ^{13}C NMR indicates the presence of an additional contribution due to Cs_1C_{60}. Since NMR is a local probe, one must conclude that Cs_1C_{60} is a very disorded phase which could not be detected in the X ray diffractogram.

TABLE I Parameters of the 3 lines detected in the ^{13}C NMR spectra of Cs_3C_{60} prepared from ammonia solution.

assignment	Cs_1C_{60} (fcc)	Cs_3C_{60} (A15)	Cs_4C_{60} (bct)
shape for sim.	Lorentzian	Lorentzian	CSA
rel. int. (%)	25 ± 5	15 ± 5	55 ± 5
$\langle\delta\rangle$ (ppm/TMS)	+178 ± 3	+199 ± 3	+180 ± 5
estim. T_1 (ms)	200	50	100

Vapor phase method

Using samples of different origins and the same experimental conditions as those described in our previous work [13] for a preparation by the vapour phase method, we were not able to obtain the same compound, whatever the presence or absence of defects. Rietveld refinement of the experimental diffraction data fits well with a mixture of a bcc Cs_6C_{60} structure together with unreacted C_{60} (Fig. 2a). Using long recycling times (up to 5 minutes), the presence of unreacted C_{60} was confirmed by ^{13}C NMR, with its characteristic line at +143 ppm *vs* TMS [27,28]. Another line of important relative intensity with its maximum at +229 ppm is attributed to Cs_6C_{60} [29].

Since an important part of C_{60} was unreacted, a sample was « in-situ » heat treated on the X ray diffractometer. Upon heating, C_{60} and bcc Cs_6C_{60} started to react together at 400°C to give a complex mixture still containing residual C_{60} (Fig. 2b). Compared to the pattern at the same temperature for the compound prepared in ammonia solution, bct and A15 phases are also identified, but there are new lines attributed to a fcc cell with a=14.24Å; the relative intensities of these lines are comparable to those of the Cs_1C_{60} phase. Taking into account the thermal expansion, the cell parameter is quite compatible with the value measured for pure Cs_1C_{60}

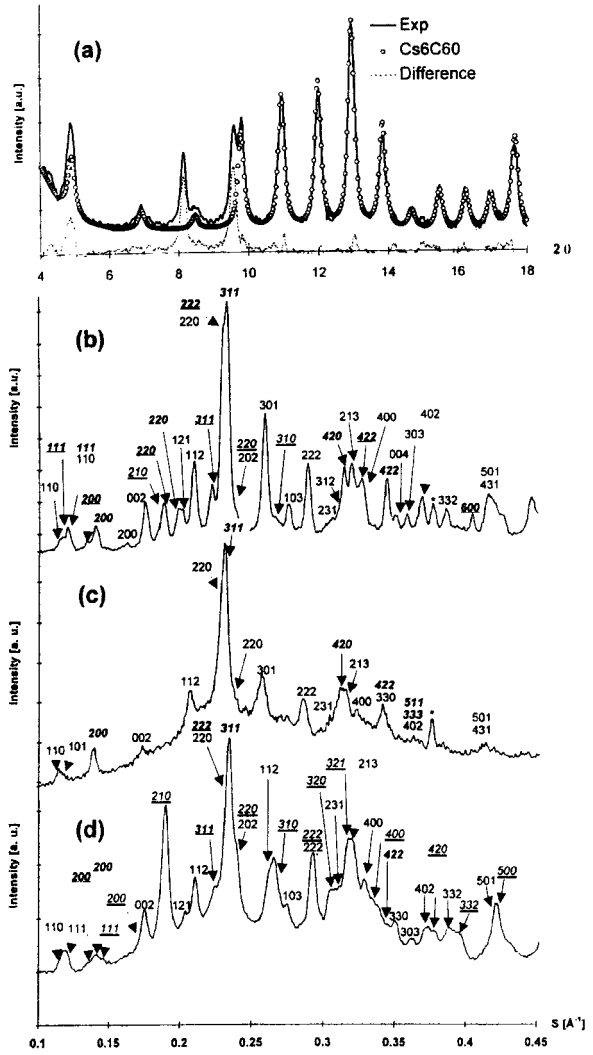

Figure 2: Diffractograms of Cs_3C_{60} prepared by the vapor phase method; (a) room temperature [experimental data: continuous line, Rietwelt fit of Cs_6C_{60}: circles, difference: dashed line]; (b) 400°C; (c) 750°C; (d) room temperature after the thermal treatment. The lines with bold indexes are attributed to Cs_1C_{60} (a=14.24Å), with normal style indexes to Cs_4C_{60} (a=b=12.38Å, c=11.4 Å), with double underlined indexes to the A15 structure (a=11.8 Å), with bold and underlined indexes to the fcc structure (a=14.88 Å).

at 200°C, i.e. 14.12Å [30]. Finally, a fcc phase (a=14.88 Å) is necessary for a complete interpretation of the diffractogram.

Up to 650°C there is not any change in the general outline of the diffraction pattern. As for the compound prepared in ammonia solution, melting of the A15 phase is achieved at 750°C, and the phases identified are bct Cs_3C_{60} and fcc Cs_1C_{60} together with a liquid (Fig 2c). After cooling down to 25°C, one can observe the reversible formation of the A15 phase but its lines are relatively more important than for the sample prepared from ammonia solution (Fig. 2d). Except the almost negligible contribution of Cs_1C_{60}, the spectrum of the vapor phase sample after heating to 750°C and cooling down to room temperature is very comparable to the one obtained by Palstra et al. from ammonia solution [18].

CONCLUSION

Pure fcc Cs_3C_{60} could not be obtained by mixing stoichiometric amounts of C_{60} and cesium. Similarly a pure bcc phase could not be reproduced. The existence of defects in pristine C_{60} do not play any role on the kind of solids formed, whatever the method used, in ammonia solution or in vapor phase. Opposite to what was claimed in some papers, heating even at high temperature does not lead to transform noticeably the solid formed in ammonia solution. In the case of the vapor phase method, heat treatment above 400°C allows to produce, after cooling down to room temperature, a material with almost the same characteristics than the one obtained from ammonia solution.

In the curve giving the relation between the lattice parameter of the fcc cell and the critical temperature [3], it is more or less assumed that the intercalation of spacer cations may lead to further enhancement of T_c. Implicitely it means that decreasing overlap between p orbitals by increasing cation diameter is responsible of a band narrowing and then of the high density at the Fermi level which produces, in the classical electron-phonon coupling model, the observed high T_c. In such a case, it is more interesting to plot the true distance between the surfaces of the neighbouring spheres which is an approximation of the distance between overlapping carbons. This curve is obtained by substracting the C_{60} diameter (7 Å) from the shortest C_{60}-C_{60} distance in each crystal (Fig. 3). It allows to explain more physically the band narrowing effect and to predict a T_c value from the crystallographic data of any kind of material. Decreasing slope of the curve gives little hope of getting a significant gain in T_c as compared to Cs_2RbC_{60} for which the intersphere distance is 3.3 Å.

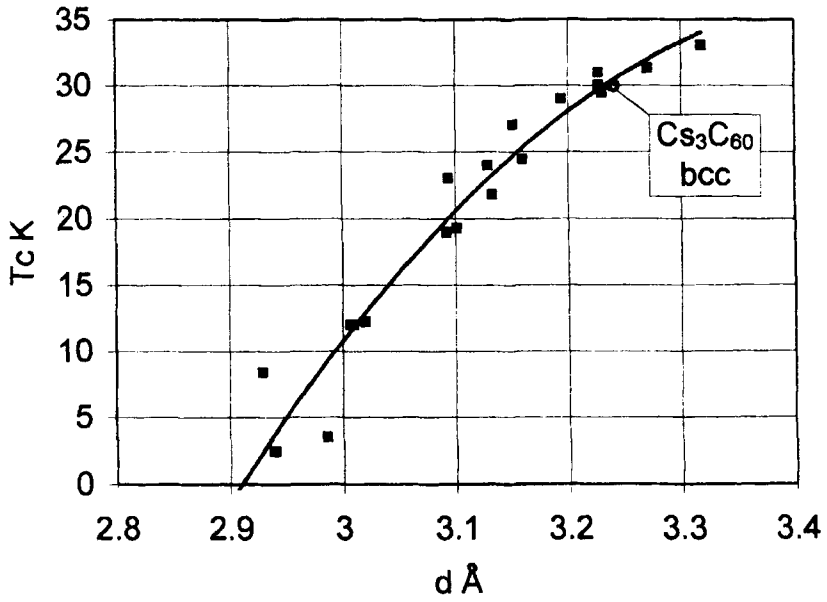

Figure 3 : Superconductivity critical temperature T_c *vs* C_{60}-C_{60} distance in various fcc M_3C_{60} phases. The distances are calculated by substracting the diameter of C_{60} from C_{60} center-C_{60} center distances in the crystal.

Such a curve appears to be more universal since it can account for other data as for example the bcc Cs_3C_{60} phase with T_c=30K and an intersphere distance of 3.24 Å [13].

The X ray pattern of this bcc phase can be described by a diluted Cs_6C_{60} phase in which 50% of the cesium positions would be occupied. Due to the fact that an apparently similar compound, especially for its superconducting properties, was obtained from CsM alloys [10], we assume that an unknown impurity present in our C_{60} samples could catalyze the formation of this compound. Since low pressure creates such a phase, it cannot be also excluded that a Cs/C_{60} ratio not exactly equal to 3 could be at its origin.

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