

Buckminsterfullerene, buckminsterfullerite and superconducting buckminsterfulleride—crystal structures

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Crystal structure analysis has become so mechanical these days that it is used routinely to solve very-large structures. However, the structures of fullerite (C_{60}) and potassium fullerenes (K_3C_{60}) have presented so many tricky problems that one is reminded of the early days of X-ray crystallography when reasoning played a vital role in the solving of crystal structures.

Buckminster Fuller conceived of the idea of geodesic domes which are extremely strong structures. These first protected World War II radars in the Arctic against snow storms and driving winds. They now enclose weather stations (even in India) and form important features of large stadia and buildings all over the world. A molecule resembling this dome made up of 60 carbon atoms has been the cause of great excitement in recent months. The original stimulus for the work which led to the hypothesis of this strange C_{60} molecule was the interest in certain features of the absorption and emission spectra of interstellar matter which defied explanation for more than half a century.

We give here some information on the crystal structure of C_{60} in the solid state as also its superconducting derivative (K_3C_{60}) mostly extracted from recent publications.

Preparation

In 1984 it was observed that carbon vapour has in it large clusters which have even numbers of carbon atoms in the range C_{40} – C_{100} . Conditions were then discovered under which the C_{60} molecules could be made to predominate in vaporized graphite. An elegant structure for this molecule was proposed based on a truncated form of one of the five platonic solids—the icosahedron. The icosahedron possesses 12 five-fold vertices, 20 triangular faces and 30 edges with two-fold rotation symmetry. In the truncated icosahedron the five-fold vertices are replaced by pentagons and the triangular faces by pseudohexagonal faces; and carbon atoms are placed at these 60 vertices. This molecule (C_{60}) is called buckminsterfullerene—a name so

long that it is either called fullerene or C_{60} . Since C_{60} molecule behaves like a single-atom entity there is a move to endow the molecule with an elemental symbol Bf! Scores of papers have already appeared on this molecule, its stability, electron energies, optical ultra-violet and infrared spectra, vibrational modes, electrical and magnetic properties, etc.

But the real advance was made when W. Krätschmer *et al.*¹ devised a simple method of extracting C_{60} from soot condensed from evaporated graphite, purifying it and getting fullerene in large quantities. The process consists of evaporating graphite electrodes in a 100-torr atmosphere of helium; collecting the material from the inside surface of the chamber and dispersing it in benzene to produce a wine-red liquid; which is then dried using gentle heat to get a residue of dark brown or black crystalline material. An alternative procedure is to sublime C_{60} at 400°C in a controlled inert atmosphere and sublimation can be done repeatedly without decomposition. Thin films or powder samples can be handled without too many special precautions and the compound appears to be fairly stable but however, over time, there seems to be some deterioration. This solid substance has been called fullerite. C_{60} can be purified by chromatography of the fullerite on octadecylsilanized silica with toluene–isopropanol eluent and dried at 160°C under vacuum.

The solid C_{60} -fullerite under an optical microscope is in the form of rods, platelet and star-like crystals (Figure 1). The crystals are reddish brown and most of them show a six-fold symmetry. Thin platelets show interference colours. Mass spectroscopy reveals a very strong peak at 720 a.m.u.

(corresponding to C_{60}). In this type of preparation the ratio of C_{70} to C_{60} is usually less than 0.1 but after repeated purification this can be reduced to 0.02. These crystals of C_{60} -fullerite are electrically insulating.

Crystal structures of fullerite

Beautiful electron diffraction patterns were obtained from the very thin micrometre-sized crystals (Figure 2). In contrast X-ray diffraction pattern from larger crystals (500 μm) with very well-developed faces yielded no clear spot pattern, indicating that there is no long-range periodicity.

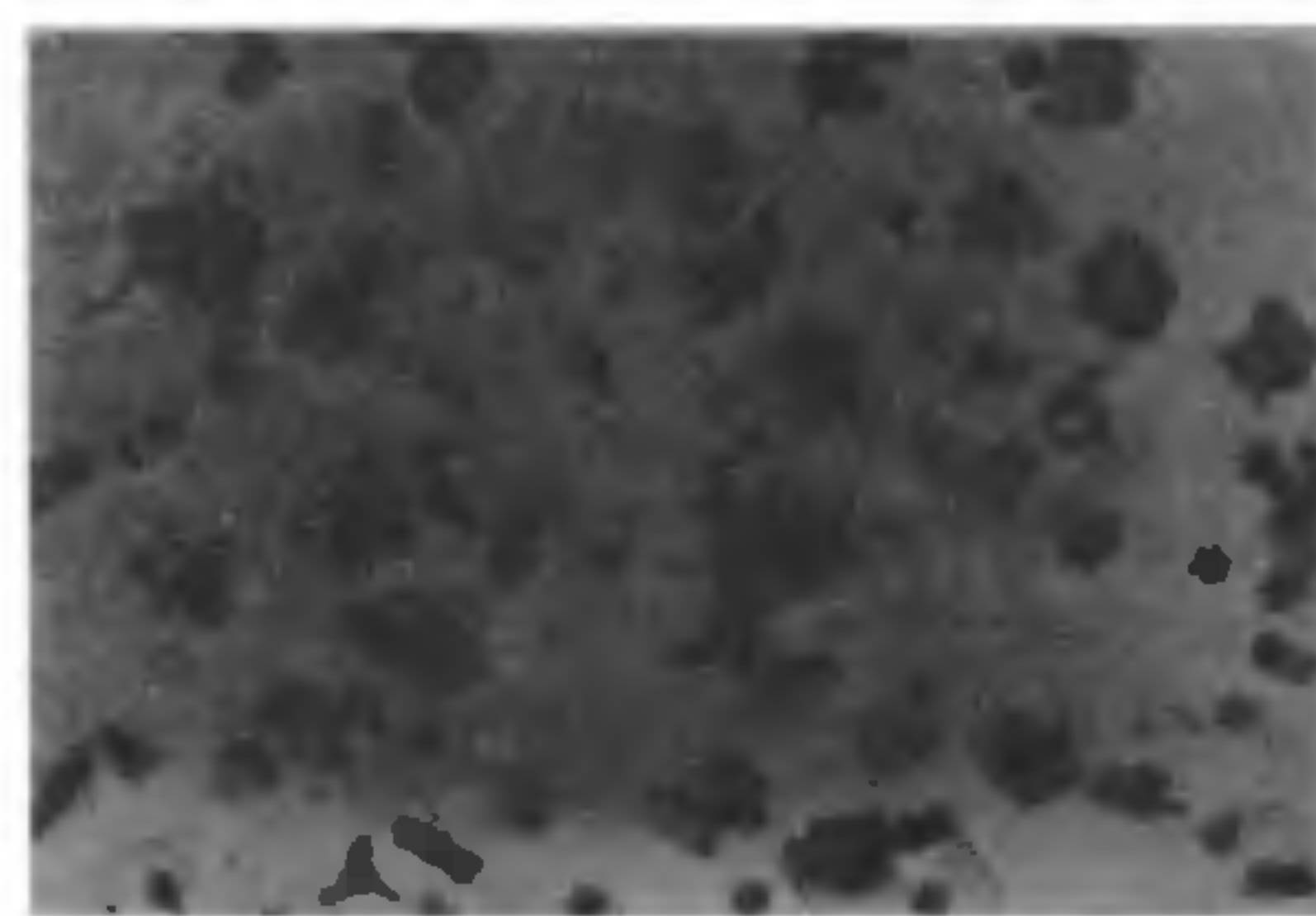


Figure 1. Typical crystals of fullerene (C_{60}) under the microscope. (From ref. 1)

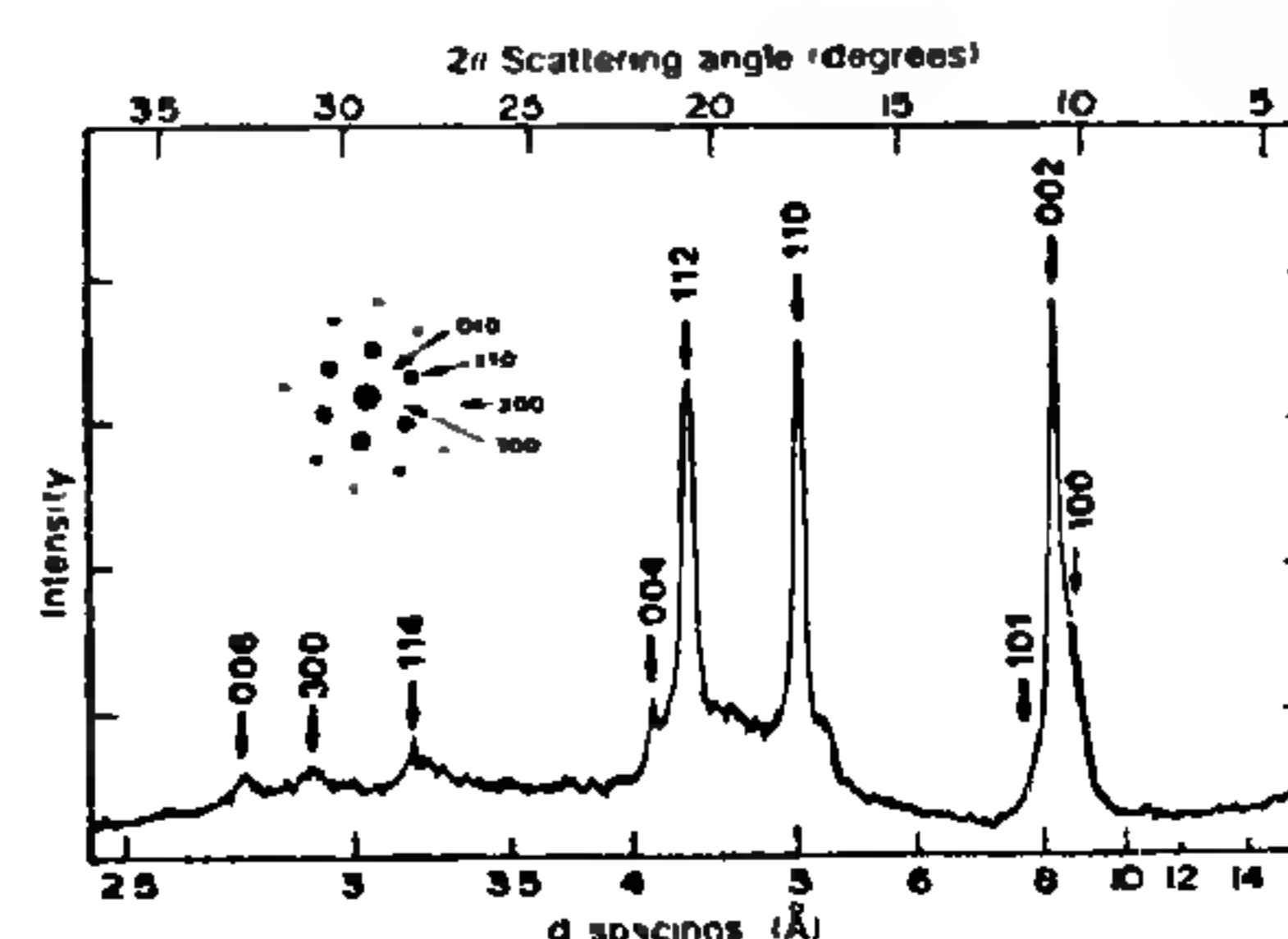


Figure 2. The first X-ray powder diagram of fullerene (C_{60}), (inset) electron diffraction pattern. Indexed as hcp lattice. (From ref. 1)

There was some difficulty in indexing the powder diffractograms (Figure 2)—whether to choose the hcp or fcc lattices. However the nearest-neighbour distance could be determined to be 10.02 Å. Assuming that fullerene molecules behave as spheres and stacked in a close-packed lattice, the density should be 1.678 g cm^{-3} which is consistent with the experimental value of $1.65 \pm 0.05 \text{ g cm}^{-3}$. Using the calculated value of cage diameter of C_{60} to be 7.1 Å and the nearest-neighbour distance as 10.02 Å, the van der Waals distance of 2.92 Å is less than the normal distance for carbon atoms (3.3 to 3.4 Å).

At room temperature, X-ray powder diffraction diagrams of fullerite show that the molecules are centred on sites of an fcc Bravais lattice, with $a = 14.17 \pm 0.01 \text{ Å}$. However, $h00$ peaks are not present despite the fact that $h00$ is allowed when h is even. At a temperature of 11 K the lattice dimension decreases to $14.04 \pm 0.01 \text{ Å}$ and many new peaks appear which can be indexed as a *simple cubic lattice* (sc) (with mixed odd and even indices which are the forbidden fcc reflections). This clearly indicates that the room temperature fcc phase has undergone a transition to a simple cubic structure. The cube edge has not however changed appreciably and so there still must be four molecules per unit cell. These four molecules which are equivalent in the fcc structure have become nonequivalent at low temperatures. This nonequivalence could be due to molecular displacements or distortions taking place at low temperatures. But model fits to the diffraction intensities indicate a strong evidence for a much simpler and more elegant explanation. At room temperature there is complete orientational disorder while at low temperatures order sets in, causing the phase change. Nuclear magnetic studies at room temperature confirms this dynamical disorder (most probably due to free rotation). NMR also shows that the disorder decreases with decreasing temperature till a complete phase change occurs when ordering is complete. The ordered phase is stable to 249 K which is considered rather high for such an ordering.

Crystal structure of K_3C_{60}

After the recent reports of superconductivity in alkali-metal-doped C_{60} , the

crystal structure of K_3C_{60} (potassium fulleride) has been determined³. An extremely pure form of superconducting K_3C_{60} could be prepared. Because of the absence of impurity phases, the structure has been determined accurately using the Rietveld analysis.

The room temperature diffraction pattern of pure fullerite (C_{60}) taken using 1.500-Å radiation and that of the fulleride (K_3C_{60}) in the superconducting phase using 0.800-Å radiation are shown in Figure 3. Both patterns correspond to fcc lattices with unit cell dimensions 14.11 Å for C_{60} and 14.24 Å for K_3C_{60} . K_3C_{60} structure can be derived from the C_{60} structure by incorporating alkali ions into the empty spaces (sites).

The largest differences in intensity between the two patterns occur in (220) and (311) reflections. Potassium ions are situated such that they interfere destructively for (220) and constructively for (311) with the carbon atoms. The potassium ions can therefore occupy sites $(1/4, 1/4, 1/4)$ and $(1/2, 0, 0)$, (Figure 4). Since stoichiometry requires three potassium ions for each C_{60} molecule the K ions *must occupy both these nonequivalent sites*, i.e. the structure is the well-known cryolite structure.

In pure fullerite (C_{60}), the spherical molecules exhibit free rotation at room temperature. In K_3C_{60} free rotation is not possible because when K ions occupy the tetrahedral and the octa-

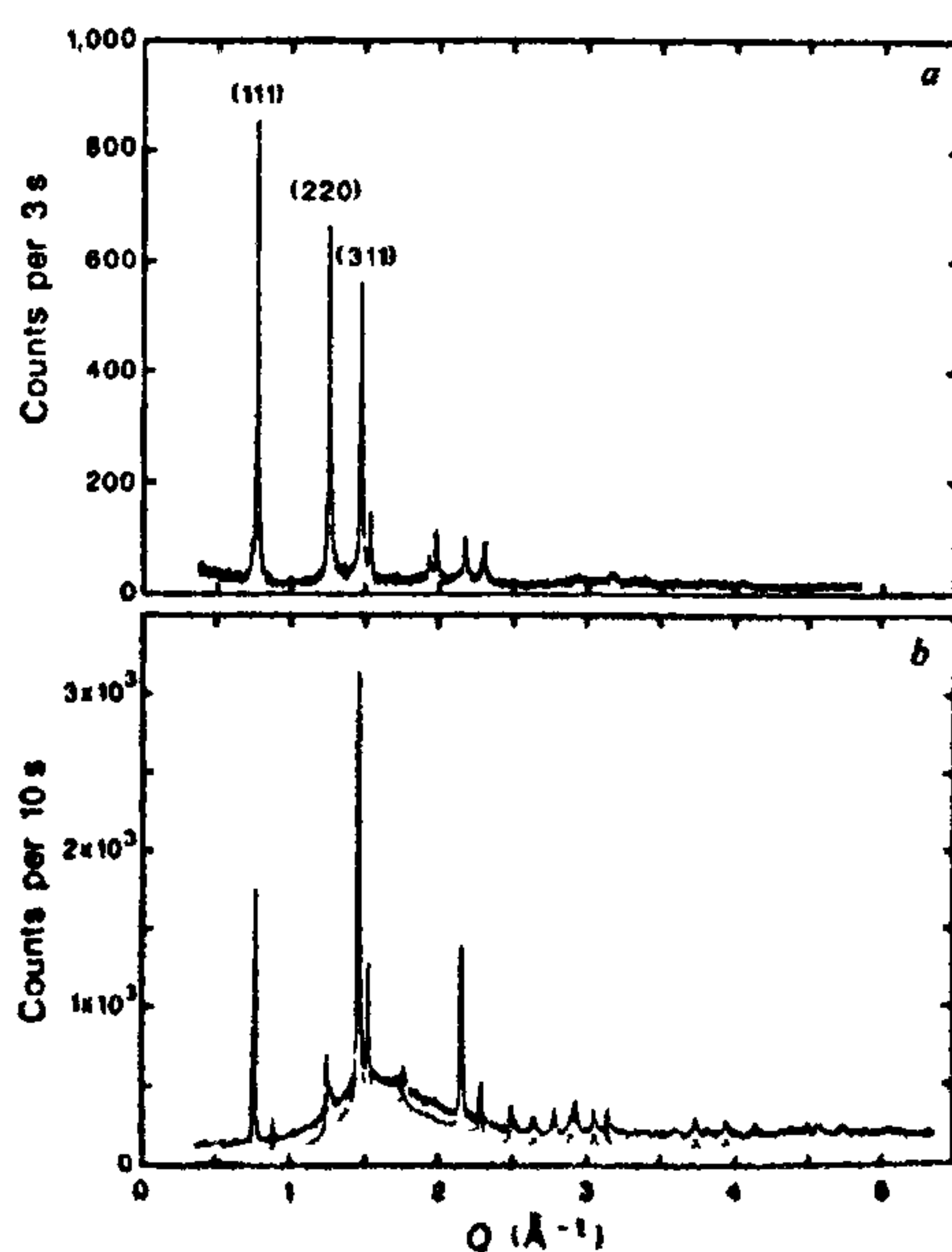


Figure 3. X-ray diffraction pattern of fullerene (a) (C_{60}) at room temperature and (b) K_3C_{60} at 11 K. Rietveld fit shown (shifted for clarity). (From ref. 3)

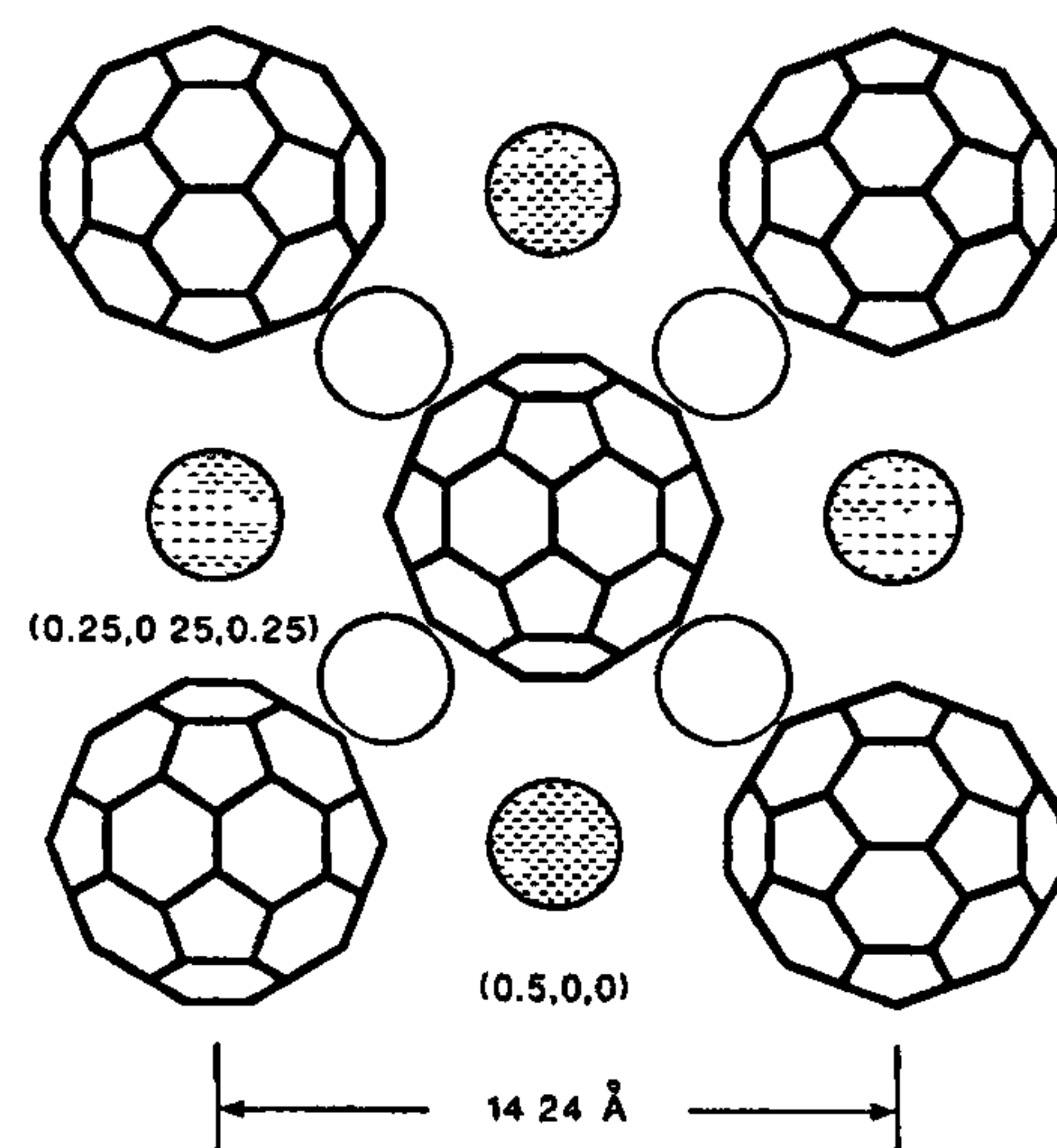


Figure 4. The structures of K_3C_{60} . Open and hatched circles represent K ions at the tetrahedral and octahedral sites respectively. Note the two orientations of the C_{60} molecule. (From ref. 3)

hedral sites the interatomic distances are too small to permit free rotation. Calculations show that there is sufficient space only for two possible orientations of the carbon molecules. The C_{60} molecule can be oriented with eight of its 20 pseudo-hexagonal faces along the (111) octahedral direction and the two possible orientations of the molecule are related by a 90° rotation about the (100) direction. The pentagons are in different positions in the two C_{60} molecules and this is illustrated in Figure 4. Rietveld refinement was done for both these cases. In the first case, C_{60} units were chosen to have the same orientation. The space group then should be $Fm\bar{3}$. For this orientation one finds that there must be a significant peak at 3.3 Å^{-1} . This is *not* observed and so one may eliminate this possibility. The second case is when the molecules are disordered between the two possible orientations stated earlier. For these the actual atomic coordinates of the C_{60} atoms can be calculated and the fit in this case is excellent (Figure 3). The space group now is $Fm\bar{3}m$ which is, of course, of a higher symmetry than that allowed for the icosahedral molecule. This can be interpreted as a 50% occupancy. Since X-ray diffraction cannot distinguish between a dynamical and frozen disorder one has to resort to NMR studies. The temperature factors of C_{60} is small enough to indicate that there is little chance for the rotation of the molecule. The larger thermal factor

for the octahedral cation indicates that larger space is available for it. The nearest C-K distance is 3.2 Å—the distance between the K ion to the nearest C atom is 3.69 Å and the closest K-K distance is 6.17 Å—much larger than in metallic K. Since the K ions occupy all the available sites in a virtually unchanged C_{60} lattice and the Rietveld fit is extremely good, it is a direct proof of the microscopic homogeneity of the material. The presence of

two crystallographically different K sites suggests that it may be possible to prepare other stable compounds. The structures of K_6C_{60} and Cs_6C_{60} which are not superconducting have also been determined. These are bcc structures with K ions in distorted tetrahedral positions.⁴

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COMMENTARY

On every occasion in recent years when Chandrasekhar gave formal and informal lectures in Bangalore, he mentioned with gratitude and affection two of his collaborators—Basilis Xanthopoulos and Valeria Ferrari. So when I read of the shocking news of the murder of Xanthopoulos in Crete by terrorists I wrote him a letter of condolence. He then sent me a little piece which was to appear along with the foreword to Volume 6 of his Selected Papers. I wrote to him 'I received the little piece that you had written in remembrance of Basilis Xanthopoulos and I noted with great sorrow the sentence "My association with Basilis is the most binding in all my 60 years of science". I realized then more than ever the incredible loss you have suffered'. I sought his permission to publish his note in Current Science which he gave. I felt that to publish Chandrasekhar's 'In remembrance of Xanthopoulos', without giving Xanthopoulos' foreword will not do full justice to the close association of the two—the teacher and the student. The foreword also gives us an inkling of Chandrasekhar's method of doing research and his attitude to science as seen by a close associate.

—Editor

In remembrance of Basilis Xanthopoulos

Basilis Xanthopoulos was shot to death in an unspeakable act of violence on the evening of 27 November 1990 while he was giving a seminar lecture on advanced computing to his senior colleagues at the Research Center of the University of Crete (Iraklion, Greece). And so ended, without warning, a life of love and joy, rich in promise.

Basilis and I collaborated on a variety of scientific subjects almost continuously from 1978, when he was a graduate student, to the present. Some of the results of that collaboration are represented in this volume. The enduring personal friendship that emerged is amply present in the warm and generous foreword that Basilis wrote for this volume (and for which I am deeply grateful).

My association with Basilis is the most binding in all my sixty years in science.

On the evening of 28 November my wife and I listened on our phonograph to the second and the third movements of the *Eroica* in a renewal of our dedication to a dear departed friend.

S CHANDRASEKHAR

Foreword to Volume 6 of S. Chandrasekhar's *Selected Papers by Xanthopoulos*

S. Chandrasekhar on black holes and gravitational waves: What a story! Forty years after his pioneer investigations, Chandra returned to the study of the dead stars. He had told us back in

1931 that massive stars could not die as ordinary objects, consisting of regular matter, could. Eddington would rebuff the idea as absurd; the scientific community would side mostly with Eddington; and, although the Schwarzschild solution was waiting around for its correct interpretation, the development of black holes would be delayed by a few decades. So, although all the ingredients

were there and we did not have to wait too long, it was not until the sixties that we would incorporate black holes into our world view.

Most of the research on the theory of black holes, including the casting of their name, occurred from the early sixties through the middle seventies. There was the discovery of the Kerr solution, the Penrose-Hawking-Geroch

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