

# Theoretical and computational study of the electron-phonon coupling in potassium-doped fullerene crystals

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## I. PURPOSE OF THE VISIT

The past 20 years have seen remarkable developments in two branches of condensed-matter physics. The first is the discovery of superconductivity in alkali-doped organic systems, notably  $K_3$ -doped fullerene [1, 2] and picene [3], which paved the way to a new research area owing to the richness of the organic chemistry and the potential exploitation of their chemical functionalization. The other is the study of strongly correlated systems with the growing realization that electronic states other than simple Fermi liquids occur in several materials families. This area has been fuelled by the potential applications of materials such as high- $T_c$  superconductors as well as by a fundamental desire to understand the ground states of interacting many-fermion systems.

This exchange visit to the Institut de Minéralogie et de Physique des Milieux condensés (IMPMC), Paris, was aimed at laying the foundation of a method working at the intersection between these two fields, starting, as a case study, from the investigation of the superconductivity in alkali-metal-doped fullerides. More in detail, the principal goal of this exchange period was to introduce the visiting researcher to the existing technology developed at IMPMC for calculating electronic structure, phonons, and electron-phonon coupling in BCS-type superconductors. This goal was reached by revisiting, under the guidance of recognized world-leading experts in this field, the previous work done on the fullerides, carrying out a state-of-the-art DFT study of the electron-phonon coupling in the potassium-doped fullerene solid. Thanks to this work, it will be possible to compute ab-initio the total coupling, for the first time converged in both the electron and phonon momenta.

IMPMC carried out a pioneering theoretical study of the superconductivity in the potassium-doped picene based on the electron-phonon coupling, computed at the density functional theory (DFT) level with Wannier interpolation [4]. There is substantial experimental evidence [3] that the mechanism inducing superconductivity in K-doped picene is phonon-driven with superconductivity appearing at a critical temperature  $T_c$  of 18 K. The properties of electron-phonon couplings in K-doped picene were analyzed by exploiting a molecular orbital representation derived in the maximally localized Wannier function formalism. This allows one to separate both the intra- and inter-molecular phonon contributions but also the local and non-local electronic states in the electron-phonon matrix elements. Despite the molecular nature of the crystal, they found out that the purely molecular coupling of the local deformation potential with intra-molecular phonons in  $K_3$ -picene accounts only for 20% of the total electron-phonon interaction  $\lambda$ . The local phonons are indeed strongly screened by the metallic bands of the doped crystal. At variance with previous hypothesis, thus, in  $K_3$ -picene superconductivity comes from non-local couplings due to phonon modulated hoppings. These findings rule out the use of molecular electron-phonon calculations to estimate the total electron-phonon coupling in metallic picene, and possibly in other doped molecular crystals, notably  $K_3$ -fullerene, completely modifying the actual explanation of superconductivity in these compounds.

The purpose of this visit was to investigate the above-mentioned scenario, put forward in the case of K-doped picene, about the possible nature of the phonon-mediated superconductivity in K-doped  $C_{60}$ , which offers the advantage to have a much more well-established and clean geometrical structure than hydrocarbon-based materials. Some experimental measurements on K-doped  $C_{60}$  powder suggest that the superconductivity in alkali-doped fullerenes can be understood in terms of the electron-phonon interaction for both K- and Rb-doped fullerene, having a  $T_c$  of 19.3 K and 28 K, respectively [5], although other experiments in Cs-doped fullerene reveal the proximity of a correlated Mott phase, signaling that strong correlation effects could be important also in the superconducting state [6]. On the theoretical side the situation is less advanced, even though quite a few model calculations were performed on the structural and electronic properties of this system [7], and on the electron-phonon coupling [8]. These studies showed that the observed superconductivity could be mediated or driven by the the strong electron-phonon coupling between the low-energy  $t_{1u}$  electronic bands with the highest frequency intra-molecular modes  $A_g$  and  $H_g$  of fullerene. In the molecular approximation, the electron-phonon coupling  $\lambda$  is factorized into the electronic interball part, setting the density of states, and local intraball phonon quantities. Other theoretical studies supported the idea that electronic

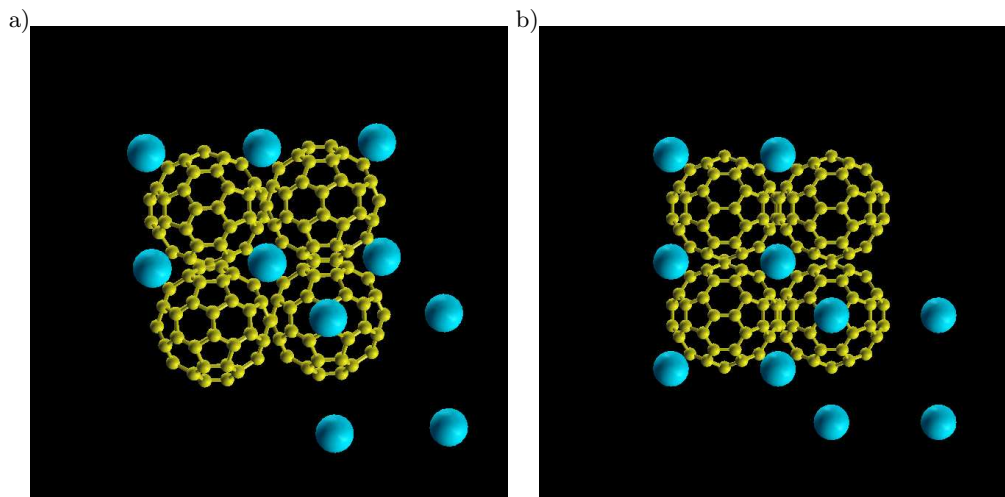


FIG. 1: The equilibrium crystal structure of  $K_3$ -fullerene in the merohedral disordered (left) and in the ordered (right) phases.

correlation is the fundamental ingredient which stabilizes the superconducting state, with the electron-phonon coupling in the molecular approximation providing the attractive channel as an effective exchange term [9].

The molecular approximation picture seems reasonable in light of the molecular nature of the loosely bound fullerenes within the fcc crystal and could be shared among all the molecular crystals presenting superconductivity. However, a full DFT calculation of the electron-phonon coupling in alkali-doped fullerenes with a detailed analysis of the different local and non-local contribution is still missing to date. In particular, the validity of the molecular approximation has never been tested against a full phonon momentum integrated electron-phonon coupling calculation from first-principles. This study, which undoubtedly represents a very interesting theoretical challenge, would allow one to make more strict conclusions on the impact of the total electron-phonon coupling, and specifically on the importance of intermolecular modes. Furthermore, it is of paramount importance in order to devise new types of carbon-based superconducting materials. This problem can be nowadays tackled by using the very recent theoretical development of the Wannier interpolation scheme, implemented in the IMPMC laboratory [10], and with the help of the outstanding HPC facilities provided by IDRIS under the GENCI Grant No. 2012096493.

## II. DESCRIPTION OF THE WORK CARRIED OUT DURING THE VISIT AND OF THE RESULTS

The first step in any *ab-initio* calculation of a real material is the assessment of the equilibrium structure. Thus, initially, we performed the structural optimization of  $K_3C_{60}$ . It is known from XRD experiment [1] that in  $K_3C_{60}$  the fullerenes occupy the sites of a fcc lattice in which two possible orientations of the  $C_{60}$  balls can occur, with the bonds shared among hexagons and pentagons oriented along the x or y axis. These two configurations are randomly oriented, giving rise to a merohedral disorder, with the crystal belonging to the  $Fm\bar{3}m$  space group. This structure is represented in Fig. 1a. In our calculations we neglected this orientational disorder, and considered the fullerenes with the same orientation (x or y) with the structure thus belonging to the  $Fm\bar{3}$  space group. The relaxed structure used in all the following calculations is represented in Fig. 1b. This assumption actually allows us to use a smaller simulation cell, containing 63 (60 C and 3 K) instead of 252 atoms. This approximation, other than mandatory for lowering the computational cost of the phonon band calculation, should not have a sizeable impact on the electron-phonon coupling except for slightly changing the hopping between the fullerenes.

However, in order to make sure that the latter approximation does not change the electronic properties, at least at the Fermi level, we performed the DOS calculations for both ordered and merohedral disordered phases. The resulting DOS's confirm the validity of our assumption (Fermi energy is shifted at 0 eV) and are plotted in Fig. 2. The *ab-initio* plane-wave calculations were performed by using the total energy and molecular dynamics Quantum Espresso package. From now onwards, thus we will refer to the orientationally ordered phase only.

In the  $K_3$ -doped fullerene crystal, potassium atoms are incorporated in two distorted tetrahedral and one octahedral interstitial sites, and play only the role of donating electrons to fullerene and increasing the lattice spacing from 14.12 to 14.24 Å with respect to the pristine fullerene crystal. Surprisingly, we discovered that the potassium atom intercalated in the highest symmetric position of the octahedral site, is not stable and a lower-energy structure exists with this potassium moved away. This has been confirmed by our phonon calculation, where we find three negative

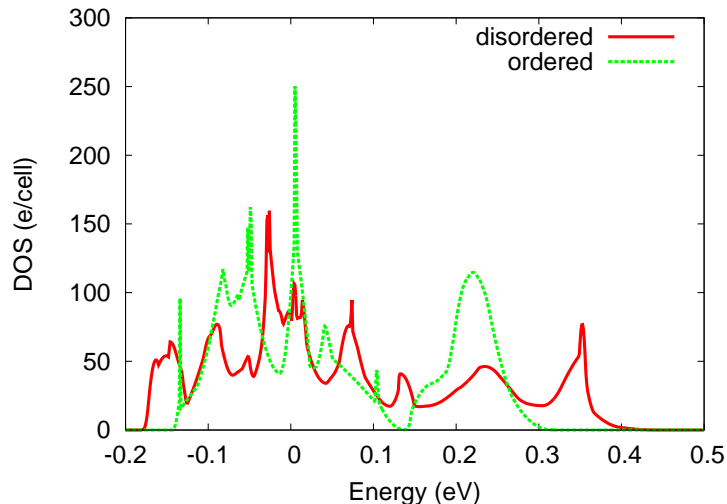


FIG. 2: Density of states of the  $K_3$ -fullerene crystal for the ordered (green dashed line) and merohedral disordered (red line) phases.

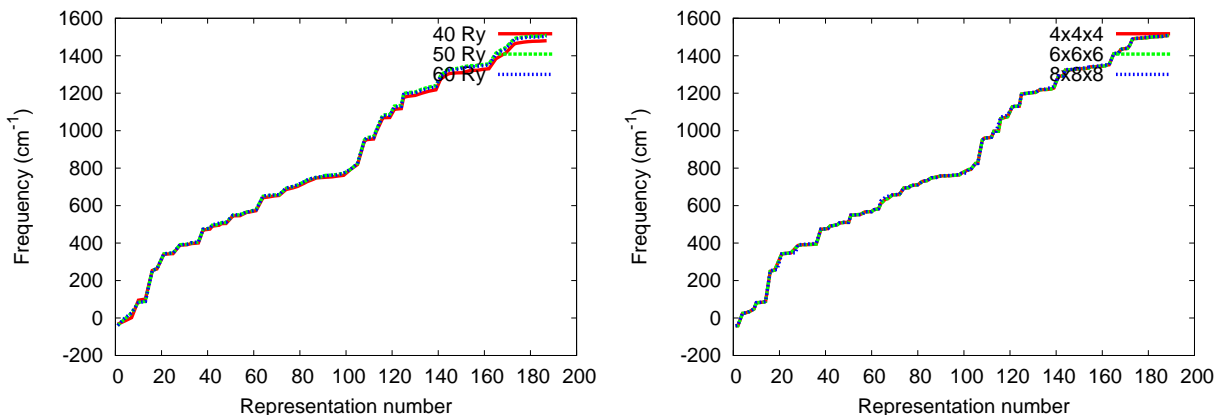


FIG. 3: Phonon frequencies as a function of the kinetic energy cut-off (left) and of the k-point grid for 50 Ry kinetic energy cut-off (right).

frequencies corresponding to such potassium instability in this configuration. Test calculations rule out a Jahn-Teller distortion mechanism as a reason of this saddle point, and the electron-phonon coupling related to these modes is negligible.

Convergence tests have been performed on both electron bands and phonon spectra (see Fig. 3 for phonons and Fig. 4 for electron bands). Finally, we decided to use the Local Density Approximation (LDA) for treating the exchange-correlation, norm-conserving pseudo-potentials for C and K to avoid convergence issues with the charge density in the phonon calculation, a kinetic energy cut-off equal to 50 Ry, and a  $4 \times 4 \times 4$  k-point grid centered at the Gamma point (reduced to 8 points by symmetry) with a Gaussian smearing of 0.003 Ry, which ensure converged results within chemical accuracy and an optimal grid for the Wannier function calculation. The number of valence bands have been reduced to 138 to save computational time and improve convergence of the phonon branches.

In Fig. 4 we report the band structure calculation for  $K_3C_{60}$  along the high-symmetry points of the fcc crystal group. As by Fig. 4 these molecular crystals, once doped, have very narrow bands of about 0.5 eV crossing the Fermi level. To better understand the interplay between the  $K_3$ -fullerene crystal geometry and the band structure, and to accurately computing the electron-phonon coupling by k-point interpolation, we want to derive a tight-binding model constructed on a Wannier basis set. Therefore, a key step is the Wannierization of the three  $t_{1u}$  bands crossing the Fermi level, which has been performed by following the procedure of Marzari and Vanderbilt [11], implemented in the Wannier90 code [12]. The usefulness of this step is twofold: firstly, it allows performing a very dense sampling in the k-integration of the coupling  $\lambda$ , owing to the Wannier interpolation; secondly, it leads to a physical interpretation

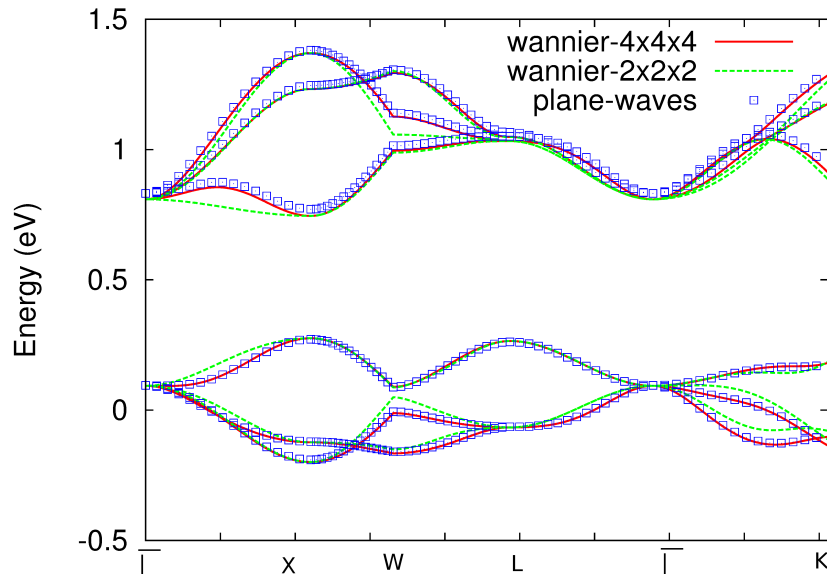


FIG. 4: Band structure of  $K_3$ -fullerene crystal at and above the Fermi level obtained from a plane-wave calculation (empty squares) and derived by Fourier-transforming a MLWF basis set (red line) including 6 states at and above the Fermi level, plotted along the  $\Gamma$ -X-W-L- $\Gamma$ -K k-space path.

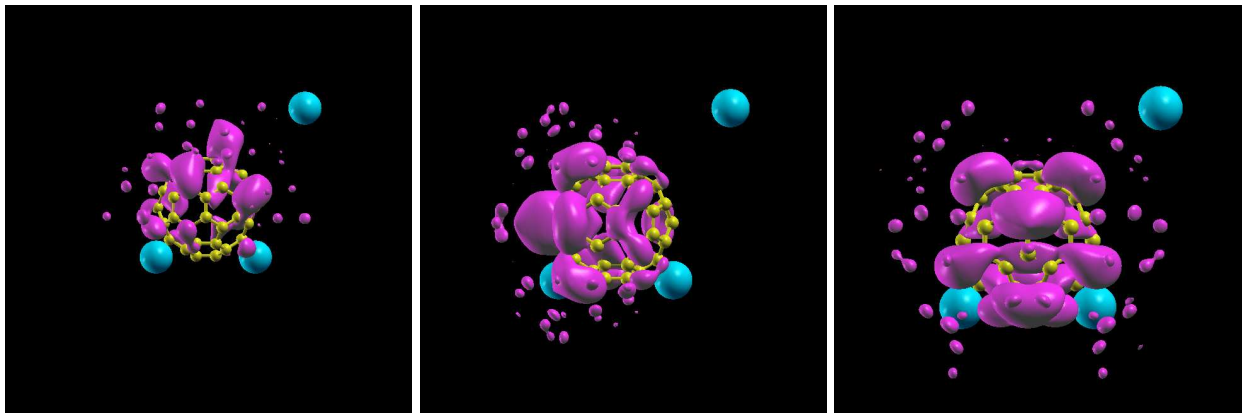
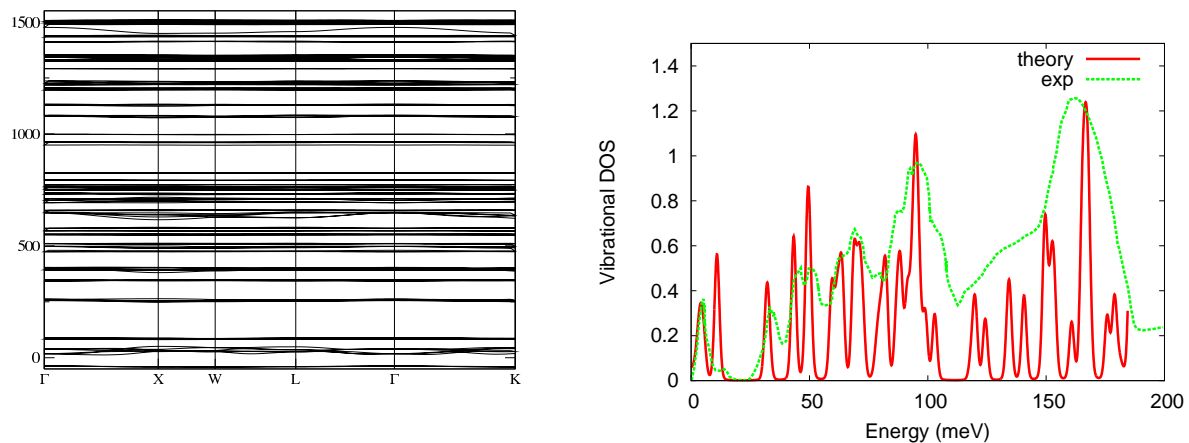
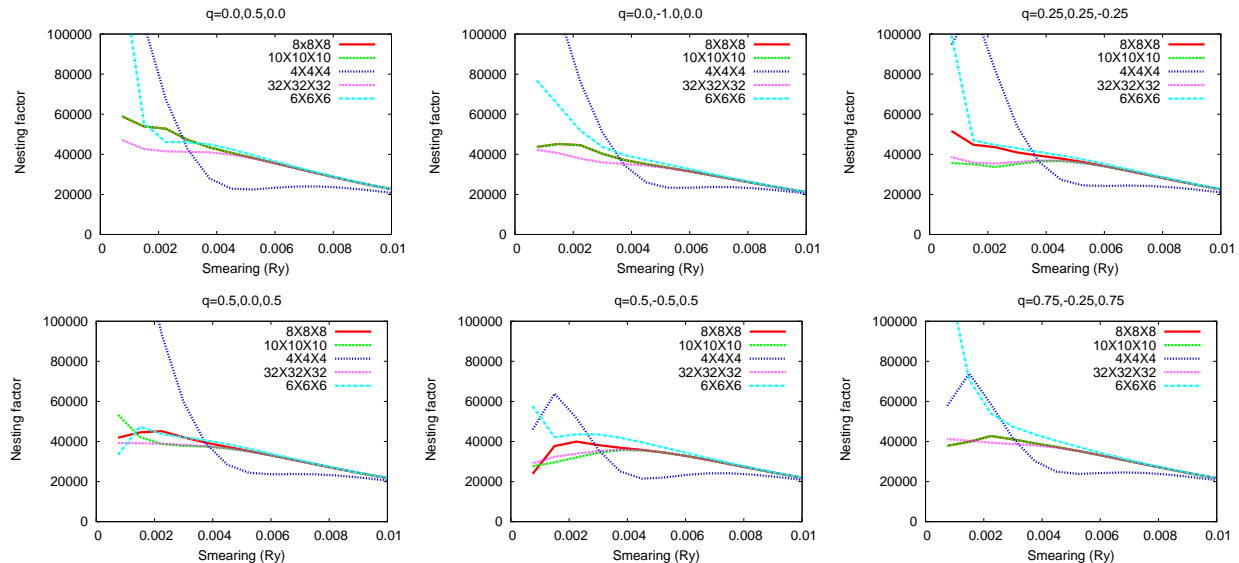


FIG. 5: Molecular maximally localized Wannier functions in real space for the  $K_3$ -fullerene crystal at the Fermi level centered on the fullerene.

of the band structure, in terms of hoppings among the localized molecular orbitals. This information can be used to derive a tight-binding Hamiltonian, which will be used in the second part of the project. In order to calculate the maximally localized Wannier functions (MLWF) we had to include both the  $t_{1u}$  bands and three higher energy bands due to the a not-so-weak entanglement of the latter with the upper bands and to use a  $4 \times 4 \times 4$  k-point grid. Therefore a preliminary disentangling procedure has been performed, before the Wannier transformation matrix can be obtained. Plots of the Wannier functions in real space and of the band dispersion at the Fermi level, obtained by Fourier-transforming back the Wannier functions to the momentum space, are reported in Figs. 5 and 4.

The second step of our work plan was the assessment of the phonon dispersion on the same  $4 \times 4 \times 4$  grid of k-points used in the previous electronic structure calculation. This is needed for the electron-phonon coupling calculation. To make sure that a fairly accurate screening in the phonon calculation is included, we have preliminarily checked the nesting factor, a quantity closely resembling the electron-phonon coupling  $\lambda$ , and related to the bare susceptibility  $\chi_0$ , for each point in the q-grid. This calculation, reported in Fig. 6, shows that a  $8 \times 8 \times 8$  k-point grid with a Gaussian smearing of 0.003 Ry is needed if one is to take into account accurately the electronic screening in the electron-phonon coupling interaction. The result of the phonon calculation, performed within the linear response density functional perturbation theory framework (DFPT) [13], is reported in Fig. 7. On the left-hand side the Fourier-interpolated

FIG. 6: Nesting factors for different q-points as a function of the Gaussian smearing ( $R_y$ ) and k-point grid.FIG. 7: Left: Phonon branches. Right: vibrational density of states of the  $K_3$ -fullerene crystal as compared to inelastic neutron scattering experiments [14] in a  $2 \times 2 \times 2$  grid of q-points for a  $8 \times 8 \times 8$  grid of k-points at 0.003 Ry Gaussian smearing.

phonon branches from a  $2 \times 2 \times 2$  q-point grid are reported in all the frequency range, from low-energy libration modes to high-energy intra-molecular C-C modes. The lowest three frequencies are found to be negative and correspond to the previously mentioned instability of potassium in the interstitial site. On the right-hand side a more insightful comparison between the vibrational DOS and the available inelastic neutron scattering data [14] is presented.

In order to complete the electron-phonon coupling two post-processing steps are still needed: the estimate of the full electron-phonon coupling of the molecular crystal, and the derivation of a low-energy model for correlated many-body calculations in fullerenes with local and non-local electron-phonon couplings (hopping). These two last steps are still the subject of further investigation.

Finally, we would like to comment on the computational cost of performing these calculations. While the ab-initio calculation of  $\lambda$  in molecular crystals are now feasible thanks to the increased computational power of the HPC facilities and to the continuous improving of the algorithms, performed even during the visit, still the computational load for the assessment of the electron-phonon coupling in a large simulation cell is very expensive in terms of both memory resources and computing time. In the specific case of  $K_3C_{60}$ , the calculation of the electronic bands - including strict convergence tests - costed around 20.000 CPU hours in a modern super-computer, while the phonon calculation costed four times as much.

### III. FUTURE COLLABORATION WITH HOST INSTITUTION

This research project has been hosted by IMPMC, where scientists interested in computational modelling of various physical phenomena routinely exchange ideas and develop novel and mutual collaborations, exploiting the methodologies used in different areas of computational science to perform state-of-the-art research in condensed matter physics, notably electron-phonon interaction and many-body theories. Furthermore, the present project overlaps with many research activities in fundamental materials science currently ongoing at the Interdisciplinary Laboratory for Computational Science in Trento, where the applicant moved from. Therefore, while the applicant spent a period of 13 weeks, just necessary to gain knowledge and to develop expertise in electron-phonon coupling calculations from first principles, the accomplishment of the outstanding tasks will certainly require further intense collaboration for the success of this project.

The first task will be to accomplish the calculation of the the electron-phonon coupling by using the Wannier interpolation procedure. On this respect, the opportunity to work in close collaboration with a group that is one of the main contributors to the Quantum-espreso total energy DFT code suite is necessary for reaching the final goal of this investigation. This was one of the particularly appealing aspects of this project, and was a new opportunity for the applicant, who gained experience in performing large-scale calculations on phonons using linear response rather than frozen-phonon approach.

As a second step, which will be part of a further collaborative effort among the two institutions, an effective low-energy model for the fullerides that includes the one-body part, and the screened couplings of the problem (local Coulomb interaction, and local and non-local electron-phonon coupling) will be derived. In perspective, this will pave the way to further studies, where correlation could be treated by many-body methods, such as dynamical mean field theory or quantum Monte Carlo, applied to the low-energy Hamiltonian. The role of correlation in the screening of phonons using different level of theory is indeed a completely new task, still unclear and debated. This further study is aimed at shedding some light on this point.

### IV. PROJECTED PUBLICATIONS / ARTICLES RESULTING OR TO RESULT FROM THE GRANT

The complexity of the electron-phonon coupling calculation in systems with large simulation cell, the required computational cost, and the post-processing of the obtained results are such that the relatively short period of time spent in Paris was just enough to set-up the working plan, perform the electronic structure DFT calculations, calculate the Wannier basis set and the phonon spectra on a 4X4X4 grid, and, finally, check it with respect to the existing experimental and theoretical data. The actual problem of the assessment of the electron-phonon coupling matrix elements has been just tackled and will be the subject of intense investigation in the nearest future. We plan to release our results as soon as possible after the accomplishment of the *ab-initio* DFT estimate of the full electron-phonon coupling of the molecular crystal and of the derivation of a low-energy model for correlated many-body calculations in fullerides with local and non-local electron-phonon couplings. This work will of course include information on all the tests performed and the results obtained on electronic structure, Wannier bands, dynamical matrix and vibrational density of states above discussed. A second work will deal with the derivation of the tight-binding model for correlated many-body calculations to assess the role of screening in the electron-phonon coupling.

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