Lattice dynamics and electron-phonon coupling in $\beta$-(BEDT-TTF)$_2$I$_3$ organic superconductor

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I. INTRODUCTION

The crystal structure and lattice phonons of (BEDT-TTF)$_2$I$_3$ superconducting $\beta$-phase (where BEDT-TTF is bis-ethylen-dithio-tetrathiafulvalene) are computed and analyzed by the Quasi Harmonic Lattice Dynamics (QHLD) method. The empirical atom-atom potential is that successfully employed for neutral BEDT-TTF and for non-superconducting $\alpha$-(BEDT-TTF)$_2$I$_3$. Whereas the crystal structure and its temperature and pressure dependence are properly reproduced within a rigid molecule approximation, this has to be removed account for the specific heat data. Such a mixing between lattice and low-frequency intra-molecular vibrations also yields good agreement with the observed Raman and infrared frequencies. From the eigenvectors of the low-frequency phonons we calculate the electron-phonon coupling constants due to the modulation of charge transfer (hopping) integrals. The charge transfer integrals are evaluated by the extended Hückel method applied to all nearest-neighbor BEDT-TTF pairs in the ab crystal plane. From the averaged electron-phonon coupling constants and the QHLD phonon density of states we derive the Eliashberg coupling function $\alpha(\omega)F(\omega)$, which compares well with that experimentally obtained from point contact spectroscopy. The corresponding dimensionless coupling constant $\lambda$ is found to be $\sim 0.4$.

74.70.Kn, 74.25.Kc
\( \beta \)-\( \text{(BEDT-TTF)}_2\text{I}_3 \) has been the first ambient pressure BEDT-TTF based superconductor to be discovered\(^2\) and its unit cell contains only one formula unit\(^2\). The BEDT-TTF radicals are arranged in stacks, and the stacks form sheets parallel to the \( ab \) crystal plane. The centrosymmetric linear \( \text{I}^+ \) anions separate the sheets, forming an insulating layer. Several variants of the \( \beta \)-\( \text{(BEDT-TTF)}_2\text{I}_3 \) phase have been reported, making difficult a full and detailed characterization. The electrochemically prepared \( \beta \)-\( \text{(BEDT-TTF)}_2\text{I}_3 \) exhibits ambient pressure superconductivity at \( T_c = 8.0 \text{ K} \) \( \beta \text{L-} \text{(BEDT-TTF)}_2\text{I}_3 \) or at \( T_c = 7.8 \text{ K} \) \( \beta \text{H-} \text{(BEDT-TTF)}_2\text{I}_3 \) depending on the pressure-temperature history of the sample. Such \( T_c \) increase has been attributed to a pressure induced ordering process of the ethylene groups of BEDT-TTF cation\(^3\). In addition, thermal treatment or laser irradiation of the \( \alpha \)-phase yields an irreversible transformation to a superconducting phase \( (T_c = 8.0 \text{ K}) \), named \( \alpha \text{-} \text{(BEDT-TTF)}_2\text{I}_3 \) which was claimed to be similar to the \( \beta \)-phase. On the other hand, \( \beta \)-\( \text{(BEDT-TTF)}_2\text{I}_3 \) can also be prepared by direct chemical oxidation \( \beta\text{CO-} \text{(BEDT-TTF)}_2\text{I}_3 \) with \( T_c \) between 7.1 and 7.8 K. Recent X-ray data confirm that thermally treated \( \alpha \)-\( \text{(BEDT-TTF)}_2\text{I}_3 \) is identical to \( \beta\text{CO-} \text{(BEDT-TTF)}_2\text{I}_3 \) but it is still not clear whether \( \beta\text{CO-} \text{(BEDT-TTF)}_2\text{I}_3 \) is the same as \( \beta \text{H-} \text{(BEDT-TTF)}_2\text{I}_3 \), the possibility of non-stoichiometric phases has also been put forward as an alternative to the ordering process in causing a \( T_c \) of about 8 K\(^4\).

The paper is organized as follows. We first discuss in some detail the methods we have adopted to calculate the structure, the phonon dynamics and the \( e-lph \) coupling strength of \( \text{(BEDT-TTF)}_2\text{I}_3 \) salts. The results relevant to the \( \beta \)-\( \text{(BEDT-TTF)}_2\text{I}_3 \) phase are then presented and compared with available experimental data. Finally, the possible role of electron-phonon coupling in the pairing mechanism of organic superconductors is briefly discussed.

## II. METHODS

### A. Quasi Harmonic Lattice Dynamics

The crystal structure at thermodynamic equilibrium of \( \text{(BEDT-TTF)}_2\text{I}_3 \) salts is computed using Quasi Harmonic Lattice Dynamics (QHLD). In QHLD\(^5\), the Gibbs free energy \( G(p,T) \) of the crystal is approximated with the free energy of the harmonic phonons calculated at the average lattice structure \( (\hbar = 1) \):

\[
G(p,T) = \Phi_{\text{inter}} + pV + \sum_{qi} \frac{\omega_q}{2} + k_BT \sum_q \ln \left[ 1 - \exp \left( \frac{-\omega_q}{k_BT} \right) \right]
\]

(1)

Here, \( \Phi_{\text{inter}} \) is the total potential energy of the crystal, \( pV \) is the pressure-volume term, \( \sum_q \omega_q/2 \) is the zero-point energy, and the last term is the entropic contribution. The sums are extended to all phonon modes of wavevector \( q \) and frequency \( \omega_q \). Given an initial lattice structure, one computes \( \Phi_{\text{inter}} \) and its second derivatives with respect to the displacements of the molecular coordinates. The second derivatives form the dynamical matrix, which is numerically diagonalized to obtain the phonon frequencies \( \omega_q \) and the corresponding eigenvectors. The structure as a function of \( p \) and \( T \) is then determined self-consistently by minimizing \( G(p,T) \) with respect to lattice parameters, molecular positions and orientations.

In the case of \( \text{(BEDT-TTF)}_2\text{I}_3 \) salts, and in particular of the \( \beta \)-phase, the choice of the initial lattice structure is somewhat problematic due to the conformational disorder of the BEDT-TTF molecules. In fact, the X-ray structural investigations\(^6\) indicate that \( \beta \)-\( \text{(BEDT-TTF)}_2\text{I}_3 \) at 120 K is disordered with two alternative sites for the terminal C atoms, labeled 9a,10a (staggered form) and 9b,10b (eclipsed form). On the other hand, \( ab \)-\( \text{initio} \) calculations\(^2\) for neutral \( \text{BEDT-TTF} \) indicate that the “boat” geometry \( (C_2 \text{ symmetry}) \) is more stable than the “planar” geometry \( (D_2 \text{ symmetry}) \) by 0.65 kcal/mole. The “chair” distortion \( (C_s \text{ symmetry}) \) is slightly more stable than the planar molecule, but still less stable than the boat one. The \( \text{BEDT-TTF}^+ \) ion is planar, and in \( \text{(BEDT-TTF)}_2\text{I}_3 \) crystals we have a statistical mixture of neutral and ionized molecules. On the basis of the site symmetry constraints, we observe that neutral molecule boat and chair geometries correspond to the Leung’s configurations 9a,10a and 9b,10b, respectively\(^2\). Thus the conformational disorder observed in most BEDT-TTF salts is readily understood: the energetic cost of deforming the molecules is small with respect to the energy gain among different packing arrangements in the crystals. To investigate at least partially the effect of conformational disorder on the stability of \( \text{(BEDT-TTF)}_2\text{I}_3 \) phases, we have performed several calculations starting from different initials molecular geometries, as detailed in Section III.
We have adopted a pairwise additive inter-molecular potential of the form $\Phi_{\text{inter}} = \frac{1}{2} \sum_{mn} [q_m q_n / r_{mn} + A_{mn} \exp(-B_{mn} r_{mn}) - C_{mn} / r_{mn}^6]$ where the sum is extended to all distances $r_{mn}$ between pairs $m,n$ of atoms in different molecules. The Ewald’s method is used to accelerate the convergence of the Coulombic interactions $q_m q_n / r_{mn}$. The atomic charges $q_m$ are the PDQ (PS-GVB) results of a recent $ab$-initio Hartree-Fock calculations, and are introduced to model both the neutral and ionized forms of the BEDT-TTF molecule. The parameters $A_{mn}$, $B_{mn}$ and $C_{mn}$ involving C, H and S atoms are taken from our previous calculation of neutral BEDT-TTF. Since in the chosen model C-H parameters are computed from C-C and H-H parameters via “mixing rules”, the same procedure is adopted here for all the interactions between different types of atoms. The iodine parameters have been derived from 9,10-diiodoanthracene, and successfully tested on $\alpha$-(BEDT-TTF)$_2$I$_3$.[14] The complete atom-atom model is given in Table I.

C. Specific Heat

The constant volume specific heat as a function of $T$ is computed directly from its statistical mechanics expression for a system of phonons:

$$C_V(T) = \sum_{q} k_B \left( \frac{\omega_{qi}}{k_B T} \right)^2 \exp \left( - \frac{\omega_{qi}}{k_B T} \right) \left[ 1 - \exp \left( - \frac{\omega_{qi}}{k_B T} \right) \right]^{-2}$$  \hspace{1cm} (2)

As usual in these cases, eq. (2) is evaluated by sampling a large number of $q$-vectors in the first Brillouin Zone (BZ).

In our first attempts to compute $C_V$, we sampled over regular grids in the BZ. We have found that for $T \leq 5$ K the statistical noise was still noticeable even after summing over several thousands of $q$-vectors; the results were dependent on the sample size. At large $T$, on the contrary, statistical convergence was quite fast. This pathology can be attributed to the fact that, due to the exponential factor in eq. (2), only the phonons with $\omega_{qi} \leq k_B T$ give a non-negligible contribution to $C_V(T)$. For very low $T$, only the acoustic branches of the phonons with $q$ close to zero have sufficiently small frequencies. With a regular grid, only a few of these vectors are sampled, and most of the computer time is wasted over regions of the BZ that are already well sampled.

To obtain accurate statistics at a reasonable cost, we have used a Monte Carlo (random) integration scheme, biased to yield a larger sampling probability close to $q = 0$. For computational simplicity, we have chosen a three-dimensional Lorentzian probability distribution, $L(q) \propto (1 + a | q |^2)^{-1}$, where $a$ is a width parameter. The bias is compensated by using the reciprocal of the sampling probability as the sample weight. With this scheme most of the computer effort is spent in the region $q \approx 0$, where a denser sampling really matters. By summing over about 2000 $q$-vectors, we have been able to reach a satisfactory statistical convergence, in the whole range between 0.1 and 20 K. At high $T$, the results coincide with those obtained by integrating over a grid. At low $T$, $C_V$ goes as $T^3$, as it should when the acoustic modes are properly sampled, and does not fluctuate with the sample size.

D. Coupling with low-frequency intra–molecular degrees of freedom

In most calculations for molecular crystals all intra–molecular degrees of freedom are neglected and the molecules are maintained as rigid units. This rigid molecule approximation (RMA) is reasonable for small compact molecules, like benzene, while normal modes have frequencies much higher than those of the lattice phonons.

Since for both I$_3^-$ and BEDT-TTF several investigations[13,14] suggest that there are low frequency intra–molecular modes, the validity of RMA for (BEDT-TTF)$_2$I$_3$ appears questionable. Therefore, we have decided to relax the RMA and to investigate the effects of the intra–molecular degrees of freedom. For this purpose we adopt an exciton-like model.[15] To start with, it is convenient to use a set of molecular coordinates $Q_i$ describing translations, rotations and internal vibrations of the molecular units in the crystal. To each BEDT-TTF molecule of $N = 26$ atoms we associate the following $3N$ coordinates: 3 mass-weighted cartesian displacements of the center of mass, 3 inertia-weighted rotations about the principal axes of inertia, and $3N - 6 = 72$ internal vibrations (the normal modes of the isolated BEDT-TTF molecule). The I$_3^-$ ion, which is linear, has 3 translations, 2 rotations and 4 internal vibrations. In order to compute the phonon frequencies, we need all derivatives $\partial^2 \Phi / \partial Q_{ri} \partial Q_{sj}$ of the total potential $\Phi$ with respect to all pairs of molecular coordinates $Q_{ri}$ and $Q_{sj}$. Here $r$ and $s$ label molecules in the crystal, while $i$ and $j$ distinguish molecular coordinates.
The potential $\Phi$ is made of intra- and inter-molecular parts, $\Phi_{\text{intra}}$ and $\Phi_{\text{inter}}$. In the exciton model, the diagonal derivatives of $\Phi_{\text{intra}}$ potential are taken to coincide with those of an isolated molecule: $\frac{\partial^2 \Phi_{\text{intra}}}{\partial Q_{ri}^2} = \omega_{ri}^2$. Here $\omega_{ri}$ is the frequency of the $i$-th normal mode of the $r$-th molecule. All off-diagonal derivatives are zero, which means no coupling among different normal modes, and no coupling between normal modes and rigid roto-translations. These assumptions are correct for the intra–molecular potential at the harmonic level (by definition).

The coupling between the molecular coordinates is given by $\Phi_{\text{inter}}$. For $\beta$-(BEDT-TTF)$_2$I$_3$, $\Phi_{\text{inter}}$ is described by atom-atom and charge-charge interactions, which are both functions only of the interatomic distance. Since the distance depends on the cartesian coordinates of the atoms, $X$, by atom-atom and charge-charge interactions, which are both functions only of the interatomic distance. Since the $X$ in terms of the coordinates $\phi$.

$\Phi_{\text{inter}}$ is the frequency of the $\text{intra}$ coupling among different normal modes, and no coupling between normal modes and rigid roto-translations. These calculations available for isolated BEDT-TTF.

Here $\phi$ describes the cartesian displacements which correspond to each molecular coordinate $Q_{ri}$. The displacements corresponding to rigid translations and rotations of the molecules can be derived by simple geometric arguments. The displacements associated to the intra–molecular degrees of freedom are the cartesian eigenvectors of the normal modes of the isolated molecule. The atomic displacements, together with the inter–molecular potential model, determine the coupling between intra–molecular and lattice modes. We remark that the intra–molecular degrees of freedom are taken into account only as far as their effects on the vibrational contribution to the free energy are concerned. No attempt to decrease the potential energy by deforming the molecules is done.

### E. $e$–$lph$ coupling constants and the Eliashberg function

In molecular crystals, intra–molecular vibrations are assumed to couple with electrons through modulation of on–site energies ($e$–$mv$ coupling). Lattice phonons are instead expected to mediate mainly the inter–molecular charge transfer (CT) integral, $e$, the corresponding linear $e$–$lph$ coupling constants being defined as:

$$g(KL; q, j) = (t_{KL} / Q_{qj})$$

where $t_{KL}$ is the CT integral between neighboring pairs KL of BEDT-TTF molecules, and where $Q_{qj}$ is the dimensionless normal coordinate for the $j$–th phonon with wavevector $q$. By relaxing the RMA, as explained above, the distinction between low–frequency intra–molecular modes and lattice modes is at least partially lost. On the other hand, $e$–$mv$ coupling by the low-frequency molecular modes is expected to be fairly small, as suggested by the calculations available for isolated BEDT-TTF. Therefore, we have assumed that the calculated low–frequency phonons of $\beta$-(BEDT-TTF)$_2$I$_3$, occurring between 0 and about 200 cm$^{-1}$, are coupled to the CT electrons only through the $e$ modulation.

To evaluate the $g(KL; q, j)$’s, we have followed a real space approach. Adopting the extended Hückel method, for each pair $K, L$ of BEDT-TTF molecules within the $\beta$-(BEDT-TTF)$_2$I$_3$ crystal we have calculated $t_{KL}$ as the variation of the HOMO energy in going from the monomer to the dimer. Such an approach is known to give $t$ values in nice agreement with those calculated by extended basis set methods. $t_{KL}$ is calculated for the dimer equilibrium geometry within the crystal, as well as for geometries displaced along the QHLD eigenvectors. The various $g(KL; q, j)$ are then obtained by numerical differentiation. We have considered only the modulation of the four largest $t$’s, all along the $ab$ crystal plane.

In the case of $e$–$mv$ coupling the overall electron-phonon coupling strength is generally expressed by the small polaron binding energy, $E_{sp}^{mv} = \sum g_i^2 / \omega_i$, where both $g_i$, the $i$–th $e$–$mv$ coupling constant, and $\omega_i$, the corresponding reference frequency, are quite naturally taken as independent of the wavevector $q$. Also in the calculation the $e$–$lph$ coupling we have assumed the optical lattice phonons as dispersionless, and have performed the calculations for the $q = 0$ eigenvectors only. Within this approximation, symmetry arguments show that only the totally symmetric ($A_g$) phonons can be coupled with electrons. Thus, the overall $e$–$lph$ coupling strength for the $j$-th lattice optical phonon, can again be expressed by the small polaron binding energy relevant to the $j$-th phonon: $\epsilon_j = \sum_{KL} (g_{KL,j}^2 / \omega_j)$. The total coupling strength is then given by $E_{sp}^{lp} = \sum_j \epsilon_j$.

For the three acoustic branches we must of course consider the $q$ dependence of the $g$’s, the coupling constants being zero for $q = 0$. We have then calculated the coupling strength ($\epsilon_{lp}^{ac}$) at some representative BZ edges in the
*b* reciprocal plane. For each branch, we have averaged the found \( e_j^a \), and assumed a linear dependence on \(|q|\). The latter assumption is correct only in the small \(|q|\) limit. The most important single parameter characterizing the strength of electron–phonon coupling in the superconductivity mechanism is the dimensionless electron–phonon coupling constant \( \lambda \). This parameter is in turn related to the Eliashberg coupling function \( \alpha^2(\omega)F(\omega) \):

\[
\lambda = 2 \int_0^{\omega_{\text{max}}} \frac{\alpha^2(\omega)F(\omega)}{\omega} \, d\omega
\]

where \( F(\omega) \) is the phonon density of states per unit cell, and \( \alpha^2(\omega) \) is an effective coupling function for phonons of energy \( \omega \). The e–lph Eliashberg coupling function can be evaluated from the QHLD phonon density of states and from the electron–phonon matrix element \( g(k, k'; j) \) expressed in the reciprocal space:

\[
\alpha^2(\omega)F(\omega) = N(E_F) \sum_j \langle |g(k, k'; j)|^2 \delta(\omega - \omega_{qj}) \rangle_{FS}
\]

where \( q = k' - k \), \( k \) and \( k' \) denoting the electronic wavevectors, and \( N(E_F) \) is the density of states per spin per unit cell at the Fermi level. In eq. (6), \( \langle \rangle_{FS} \) indicates the average over the Fermi surface.

We have calculated the \( g \)'s in real space, as detailed above. In order to introduce the dependence on the electronic wavevector \( k \), as required in eq. (6), we have to describe the electronic structure of the \( \beta \)-phase metal. To get a simple yet realistic model we make resort of the rectangular tight–binding dimer model, where the BEDT-TTF dimers inside the actual unit cell are taken as a supermolecule. Actually, as in \( \kappa \)-phase, in the \( \beta \)-phase structure BEDT-TTF dimers are clearly recognized (in the present formalism, they correspond to the \( t_{KL} \) CT integral). In this model there is only one half–filled conduction band in the first BZ, whose dispersion relation as a function of the \( t_{KL} \) CT integrals is easily obtained:

\[
\epsilon(k) = t_{AB} + t_{AH} \cos(k_x) + t_{AE} \cos(k_y) + t_{AC} \cos(k_x + k_y)
\]

The chemical potential is obtained numerically from the half–filling condition. Within our tight–binding approximation, the dependence in reciprocal space of the coupling constants associated to the inter–dimer (inter–cell) hoppings is given by:

\[
g(k, k'; j) = 2i \, g(KL; q, j) [\sin(k + q)R - \sin kR]
\]

where \( R \) represents the nearest–neighbor lattice vectors \((a, b, a + b)\), and \( g(KL; q, j) \) are the three corresponding real space inter–cell CT integrals. The Fermi surface average of eq. (6) can now easily performed numerically for the inter–dimer contribution. The coupling constants associated with the modulation of the inter–dimer CT integrals are treated as intramolecular coupling constants, and as such are independent of \( k \). We finally remark that the e–mv Eliashberg coupling function is simply given by \( [\alpha^2(\omega)F(\omega)]_{e-mv} = (N(E_F)/N) \sum_i g_i^2 \delta(\omega - \omega_i) \) \( N \) being the number of molecules per unit cell and \( g_i \) being the usual e–mv coupling constant so that \( \lambda_{e-mv} = N(E_F)E_{sp}^{mv} \).

### III. RESULTS

#### A. Crystallographic structures

The unit cell of \( (\text{BEDT-TTF})_2\text{I}_3 \) contains one \( \Gamma_1 \) ion at the \( 000 \) inversion site and two BEDT-TTF molecules at generic sites. At 4.5 K the two BEDT-TTF molecules have a boat geometry (with the terminal C atoms in 9a,10a positions) and are interconverted by the inversion. At 100 and 120 K the lattice is disordered and inversion symmetry is satisfied only statistically, with a mixture of boat and chair molecules.

As explained in section II, at first we have made calculations with rigid molecules, and then we have relaxed the RMA with the addition of a subset of intra–molecular modes. The crystal structure is only marginally affected by RMA and in Table II we report the comparison between RMA-calculated and experimental crystal structure at several temperatures and pressures. Fig. 1 reports a more extensive and direct comparison between calculated and experimental crystal axis lengths against \( T \) and \( p \). The calculations have been performed by minimizing the free energy.
changes in molecular geometry, the structures of \( \beta \)-\( \text{(BEDT-TTF)} \)\(_2\text{I}_3 \) have been recomputed with the 120 K geometry and ordered molecules (staggered or boat form). The effect of the change in molecular geometry is negligible. At all temperatures, \( \beta \)-\( \text{(BEDT-TTF)} \)\(_2\text{I}_3 \) appears to be thermodynamically more stable than \( \alpha \)-\( \text{(BEDT-TTF)} \)\(_2\text{I}_3 \) giving account for the irreversible interconversions of \( \alpha \)-(BEDT-TTF)\(_2\text{I}_3 \) into \( \beta \)-like phases.

The effect of molecular deformations has been investigated, within the RMA approximation, by testing several model geometries in \( \beta \)-(BEDT-TTF)\(_2\text{I}_3 \) as well as in \( \alpha \)-(BEDT-TTF)\(_2\text{I}_3 \) phases. The potential energy has been minimized with the experimental geometries \(^{27,28,29} \) and with chair-\( \alpha \), chair-\( \beta \), boat-\( \alpha \), and boat-\( \beta \) model geometries. The chair-\( \alpha \) geometry is the average of the two chair molecules in \( \alpha \)-(BEDT-TTF)\(_2\text{I}_3 \) while chair-\( \beta \) is the molecule of \( \beta \)-(BEDT-TTF)\(_2\text{I}_3 \) with all the terminal carbons in \( 9b,10b \) positions \(^{28} \). The boat-\( \alpha \) and \( \beta \) geometries are those observed in the corresponding phases \(^{27,28,29} \). For both \( \alpha \) and \( \beta \) phases, the potential energy minimum is found with experimental geometry of that phase, and the system becomes less stable if any other geometry is used. It should be noticed that for \( \beta \)-(BEDT-TTF)\(_2\text{I}_3 \) the boat-\( \beta \) geometry coincides with the experimental geometry at 4.5 K, and thus yields the lowest energy. The difference between \( \alpha \)-(BEDT-TTF)\(_2\text{I}_3 \) and \( \beta \)-(BEDT-TTF)\(_2\text{I}_3 \) essentially vanishes if the chair-\( \alpha \) and boat-\( \alpha \) geometries are used in the \( \beta \)-phase, while the chair-\( \beta \) and boat-\( \beta \) geometries drastically destabilize the \( \alpha \)-phase. This behavior clearly indicates that molecular deformations play a crucial role in stabilizing the various \( \text{(BEDT-TTF)} \)\(_2\text{I}_3 \) phases.

**B. Specific heat**

We next turn our attention to the phonon structure. In the \( \beta \)-phase we have only one formula unit in the triclinic unit cell, and within RMA we expect 8\( A \) and 6\( A_u \) \( q = 0 \) lattice phonons active in Raman and in IR, respectively. The number of phonons experimentally observed in the 10-150 cm\(^{-1} \) spectral region is in any case smaller than the above prediction, so vibrational spectra do not offer a very stringent test of the calculations. On the other hand, there is another observable, the specific heat, which depends on the frequency distribution. As shown in Fig. 2, at 20 K the \( C_V \) calculated within RMA (dotted line) is about 50% smaller than the experimental \( C_p \) (dots, from Ref. \(^{33} \)). The difference between \( C_V \) and \( C_p \) is usually small for solids, since their thermal expansion is small. Therefore, we attribute most of the discrepancy between \( C_V \) and \( C_p \) to the \( \text{intra-} \)molecular modes, which are neglected in the RMA calculation.

\( \text{Ab-initio} \) calculations \(^{33,34} \) indeed indicate the presence of several low-frequency BEDT-TTF \( \text{intra-} \)molecular (internal) normal modes. Since calculations refer to a free molecule, a direct comparison with experimental data in the solid state is not feasible. However, they constitute a very convenient starting point for relaxing RMA in QHLD calculations, as explained in Section II. We have included the lowest nine BEDT-TTF internal modes which fall in the same spectral region as the lattice modes (below \( \sim \) 220 cm\(^{-1} \)), and therefore are likely coupled. In addition, the symmetric and antisymmetric stretchings, and the two bendings of \( I_3 \), expected at 114, 145, 52 and 52 cm\(^{-1} \), respectively \(^{39,40} \), have been included in the QHLD calculations. The cartesian displacements of BEDT-TTF were obtained from the \( \text{ab-initio} \) calculations \(^{34} \) while those of \( I_3 \) were determined by symmetry alone, as often it happens for small molecules with high symmetry.

The \( C_V \) computed by relaxing the RMA is also shown in Fig. 2. The agreement with experiment is greatly improved with respect to RMA calculations. We anticipate that the same kind of result has been obtained for \( \kappa \)-(BEDT-TTF)\(_2\text{I}_3 \) \(^{34} \) and conclude by stating that RMA has to be relaxed for a realistic calculation of the low-frequency phonons of BEDT-TTF crystals.

**C. Phonon assignments**

We now go back to the characterization of individual low-frequency phonons. In the RMA classification, below 220 cm\(^{-1} \) we expect Raman activity for 8 lattice modes, 9 BEDT-TTF \( \text{intra-} \)molecular modes and one stretching of \( I_3 \); in IR we expect 6 lattice modes, 9 BEDT-TTF \( \text{intra-} \)molecular modes and three \( I_3 \) modes. The modes calculated at the minimum \( G \) structure at 120 K are compared with experimental ones in Tables III and IV for \( A_\alpha \) and \( A_\gamma \) modes, respectively. We have chosen the 120 K temperature since in this way we can compare the normal state phonon frequencies and eigenvectors for the minimum \( G \) and the experimental \( G \) structure. The frequency differences between minimum \( G \) and experimental structure are quite small. The comparison between calculated and experimental vibrational frequencies is satisfactory, although not very significant given the low number of observed frequencies. Since we also have all the corresponding eigenvectors, we report an approximate description of the phonons, given for both BEDT-TTF and \( I_3 \) as percentage of the lattice (rigid molecule) and of the \( \text{intra-} \)molecular contributions.
Since in some cases there is a considerable mixing between lattice and molecular modes, a clear distinction cannot be made. Fig. 3 reports the full dispersion curves along the C, V, X, and Y directions and density of states of $\beta$-(BEDT-TTF)$_2$I$_3$. In order to make the figure more readable, we have limited the highest frequency to 150 cm$^{-1}$. Fig. 3 puts in evidence the complex structure of $\beta$-(BEDT-TTF)$_2$I$_3$ low-frequency phonons. We have a very dense grouping of modes in the 50-100 cm$^{-1}$ region, with several avoided crossings between the dispersion curves, and clear mixing between lattice and molecular modes. Only the acoustic phonon branches contribute to the density of states below $\sim$ 25 cm$^{-1}$, so that the typical $\omega^2$ dependence is observed. On the other hand, at energies higher than $\sim$ 140 cm$^{-1}$ the almost dispersionless intra-molecular modes dominate, and the phonon density of states appears as a sum of delta-like peaks (not shown in the figure).

D. Electron-phonon coupling

The $e$--lph coupling constants for the optical phonons of $\beta$-(BEDT-TTF)$_2$I$_3$ are reported in Table IV. As explained in Section II, if one assumes that the eigenvectors are independent of $q$, only the $A_1$ phonons can couple to electrons. In Table IV for each phonon we report both the individual $g(K; j, q)$ (Eq. 5) and the small polaron binding energy $\epsilon_j$. The two most strongly coupled modes are those calculated at 32 and 113 cm$^{-1}$. Whereas the former mode has been observed in the Raman spectrum, and together with the lower frequency mode (27 cm$^{-1}$) undergoes a drastic intensity weakening at $T_c$, the latter has not been reported even in the normal state. The reason might be due to the proximity of the very intense, resonantly enhanced band at 121 cm$^{-1}$, due to the symmetric stretch of the I$_3^-$ anion. One band at 107 cm$^{-1}$ has been observed below 6 K for 488 nm laser excitation. On the other hand, a band at 109 cm$^{-1}$ whose intensity varies with sample and irradiation, has been attributed to the splitting of the I$_3^-$ stretching mode as a consequence of the commensurate superstructure reported in one X-ray investigation at 100K. Certainly the 100-130 cm$^{-1}$ spectral region deserves further experimental scrutiny with the latest generation of Raman spectrometers. A second observation is that whereas the 113 cm$^{-1}$ mode involves only the BEDT-TTF units, and is mostly a lattice mode, the 32 cm$^{-1}$ one is a mixing between rigid I$_3^-$ motion and “flexible” BEDT-TTF vibrations. This finding suggests a not marginal role of the counter-ions sheets in $\beta$-type BEDT-TTF salts.

As shown by Table IV, the coupling of individual optical modes with electrons is in general not particularly strong, but on the whole the strength of $e$--lph coupling, as measured by the sum of the $\epsilon_j$, is appreciable, around 45 meV, to which we have to add the contribution of the acoustic phonons. For the sake of comparison, we give also the $\epsilon_{ac}^j$ for the three acoustic branches, calculated as average over several points at the BZ edges. In order of decreasing phonon frequency (see Fig. 3) the $\epsilon_{ac}$ are: 2.3, 3.3 and 18.2 meV, respectively. The coupling strength of the lowest acoustic branch at the zone edge is comparable to that of the most strongly coupled optical phonons. Thus the overall $e$--lph coupling strength is of the same order of magnitude as that due to $e$--mv coupling, about 70 meV.

We can make a more direct connection with superconducting properties by calculating the Eliashberg function and the dimensionless electron-phonon coupling constant $\lambda$. As seen in eq. (6), the absolute value of the Eliashberg function depends on the electronic density of states at the Fermi energy, $N(E_F)$. Experimental estimates of this critical parameter are problematic, since the measured quantities already include or the $\lambda$ enhancement factor, or the Coulomb enhancement factor, or both. The available theoretical estimates are all based on the extended Hückel tight binding method. The choice of $N(E_F) = 2.1$ spin states/eV/unit cell, as obtained by this method, is consistent with our extended Hückel estimates of the CT integrals in real space. To our advantage, we can compare the calculated $\alpha(\omega)F(\omega)$ with that derived from normal state current/voltage measurements at a point contact junction. This kind of experiment is rather difficult to perform on organic crystals like $\beta$-(BEDT-TTF)$_2$I$_3$, since one has to be careful about pressure effects at the point contact. The use of a contact between two $\beta$-(BEDT-TTF)$_2$I$_3$ crystals made the current-voltage characteristics rather stable, from which the $\alpha(\omega)F(\omega)$ function reported in the upper part of Fig. 4 was obtained. We have changed the scale on the ordinate axis to maintain the same energy unit (cm$^{-1}$) throughout. It is clear that the spectral resolution of the experiment is larger than $\sim$ 10 cm$^{-1}$, and probably increases with energy. Indeed, no spectral detail is visible beyond 240 cm$^{-1}$, where the contribution of $e$--mv coupled modes should be detectable. Therefore, to make easier the visual comparison with the experimental data, we have smoothed the calculated $\alpha(\omega)F(\omega)$ (Fig. 4, lower part) by a convolution with a Gaussian distribution. We have also assumed that the Gaussian distribution width increases linearly with $\omega$ (from 0.1 to 20 cm$^{-1}$ in the 1-200 cm$^{-1}$ interval).

Fig. 4 puts in evidence the very good agreement between experiment and calculation. The absolute scale of $\alpha(\omega)F(\omega)$ turns out to be practically the same, even if both experiment and calculation are affected by considerable uncertainties, as explained above. The three main peaks observed in the experiment are well reproduced and are identified as due to the most strongly coupled phonon branches, namely, the optical phonons at 113 and 32 cm$^{-1}$, and the lowest frequency acoustic branch. The calculated peak frequency due to the latter is slightly higher than the experimental one (22 vs 10 cm$^{-1}$). This discrepancy might be due to the fact that the experiment refers to the $\beta_L$-
(BEDT-TTF)$_2$I$_3$ phase, whereas our calculation refers to a perfectly ordered phase like the $\beta^*$-(BEDT-TTF)$_2$I$_3$. We also remark that, at variance with traditional superconductors, the Eliashberg function is remarkably different from the phonon density of states (Fig. 3). For instance, the peak around 120 cm$^{-1}$ in $F(\omega)$ is due to the dispersionless $\Gamma_3$ stretching mode, which is completely decoupled from the electron system, whereas the broad peak in $\alpha(\omega)F(\omega)$ is due to the nearby (113 cm$^{-1}$) “lattice” mode of the BEDT-TTF molecules. Due to the complex phonon structure, $\alpha(\omega)$ is not nearly constant, but varies rapidly with the frequency.

The dimensionless coupling constant $\lambda$ obtained by integration of $\alpha(\omega)F(\omega)/\omega$ up to 240 cm$^{-1}$ turns out to be around 0.4. The contribution to $\lambda$ from $e$–mv coupled modes is instead around 0.1. Thus in the McMillan picture the overall $\lambda$ of $\beta$-(BEDT-TTF)$_2$I$_3$ is $\sim$ 0.5, which may well account for the observed $T_c = 8.1 \text{ K}$.}

IV. DISCUSSION AND CONCLUSIONS

The computational methods we have adopted to analyze the crystal and lattice phonon structure, and the electron-phonon coupling strength of $\beta$-(BEDT-TTF)$_2$I$_3$ are empirical or semiempirical. The form of QHLD atom–atom potentials has no rigorous theoretical justification, and the corresponding parameters are derived from empirical fittings. We have adopted ab–initio atomic charges to take into account Coulomb interactions between atoms, and ab–initio vibrational eigenvectors to introduce the coupling between lattice and molecular modes. Also the extended Hückel method used to characterize the $\beta$-(BEDT-TTF)$_2$I$_3$ electronic structure is semiempirical, albeit with an experimental basis far wider than QHLD. In view of the obvious limitations of empirical or semiempirical methods, the success achieved in the case of $\beta$-(BEDT-TTF)$_2$I$_3$ is even beyond our expectations, also considering that none of the empirical parameters has been adjusted to fit $\beta$-(BEDT-TTF)$_2$I$_3$ experimental data.

Indeed, all the available $\beta$-(BEDT-TTF)$_2$I$_3$ experimental data have been accounted for. The crystal structure, and its variation with temperature and pressure, is correctly reproduced (Fig. 1 and Table II). Useful hints about the relative thermodynamic stability of (BEDT-TTF)$_2$I$_3$ $\alpha$ and $\beta$ phases have been obtained, as well as some indications on the effect of BEDT-TTF conformation of the phases stability. The specific heat (Fig. 2) and the few detected Raman and infrared bands have been accounted for by including the coupling with low-frequency molecular vibrations. Finally, the point contact Eliashberg spectral function has been satisfactorily reproduced (Fig. 4).

Despite the success, it is wise to keep in mind the QHLD limitations. First and foremost, conformational disorder in the crystal structure is not included. This is not a limitation of the QHLD method only, but it is a serious one particularly for $\beta$-(BEDT-TTF)$_2$I$_3$ salts, where disorder plays an important role even in the superconducting properties. It is in fact believed that a fully ordered structure is at the origin of the higher $T_c (8.1 \text{ K})$ displayed by $\beta^*$- or $\beta_H$- phases with respect to $\beta_L$-(BEDT-TTF)$_2$I$_3$ (1.5 K). Furthermore, even if the QHLD method is able to follow the $T$ and $\rho$ dependence of the crystal structure, phase transitions implying subtle structural changes may be beyond its present capabilities, even for fully ordered structures. The relative stabilities of the phases can indeed be reproduced only at a qualitative level. For what concerns the electron-phonon coupling, one has to keep in mind that it depends on phonon eigenvectors, and these are obviously more prone to inaccuracies than the energies. Finally, extension to other BEDT-TTF salts with counter-ions different from I$^-$ is not obvious, requiring additional atom-atom parameters.

Once the above necessary words of caution about the method are spelled out, we can underline what in any case have learned from the present QHLD calculations. So far, in the lack of any description, no matter how approximate, of the phonons modulating the CT integrals, only speculative discussions about their role in the superconductivity could be put forward, catching at best only part of the correct picture. One of the most important indications coming out from the present paper is the need of relaxing the RMA. So from one side we cannot try to focus on the isolated molecule intra–molecular vibrations presumably modulating the CT integral, and on the other side that the “librations” of the rigid molecule lack of precise meaning. In other words, there is no simple or intuitive picture of the phonons modulating the CT integrals. Our results, and the overall mode mixing, suggest that also the counter-ions vibrations may play a perhaps indirect role in the coupling.

The results of the present paper definitely assess the very important role played by the low-frequency phonons in the superconducting properties of BEDT-TTF salts. Both acoustic and optic modes modulating the CT integral are involved. The overall dimensionless coupling constant is $\sim$ 0.4, much larger then that due to it e–mv coupled phonons ($\sim$ 0.1). Of course, a mere numerical comparison of the two $\lambda$s is not particularly significant, since one has to keep in mind the very different time scales (frequencies) of the two types of phonons. The phonons appreciably modulating the CT integrals fall in the 0-120 cm$^{-1}$ spectral region (Table IV), whereas those modulating on-site energies have frequencies ranging from 400 to 1500 cm$^{-1}$. Applicability of the Migdal theorem to the latter appears dubious: non-adiabatic corrections or alternative mechanisms such as polaron narrowing have been suggested. For these reasons we will not get involved into detailed discussions about the relative role of $e$–lph and $e$–mv coupling in the
superconductivity mechanism. We limit ourselves to state that phonon mediated coupling can well account for the observed critical temperature of the ordered $\beta$-(BEDT-TTF)$_2$I$_3$ phase, given plausible values of the other fundamental parameter, the Coulomb pseudopotential $\mu$.

The results of the present paper suggest that phonon mediated mechanism is responsible for the superconductivity of BEDT-TTF-based salts. The same conclusion was reached on the basis of the solution of the BCS gap equation for $\kappa$ phase BEDT-TTF salts. On the other hand, evidences are also accumulating towards non-conventional coupling mechanisms in organic superconductors, such as spin-fluctuation mediated superconductivity. Similar apparently contrasting experimental evidences are also found for cuprates pointing to a superconductivity mechanism where both electron-phonon coupling and antiferromagnetic spin correlations are taken into account.

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TABLE I. Parameters for the atom-atom potential $V_{ij}(r) = A_{ij} \exp(-B_{ij}r) - C_{ij}/r^6$. $V$ is in kcal/mol, $r$ in Å, $A$, $B$, $C$ in consistent units. Heteroatom parameters are given by $A_{ij} = \sqrt{A_{ii}A_{jj}}$, $B_{ij} = (B_{ii} + B_{jj})/2$ and $C_{ij} = \sqrt{C_{ii}C_{jj}}$.

| $i$ | $A_{ii}$ | $B_{ii}$ | $C_{ii}$ |
|-----|----------|----------|----------|
| H   | 2868     | 3.74     | 40.2     |
| C   | 71460    | 3.60     | 449.3    |
| S   | 329600   | 3.31     | 5392.0   |
| I   | 642376   | 3.09     | 16482.6  |

TABLE II. Structural data of $\beta$-(BEDT-TTF)$_2$I$_3$ as a function of $T$ (K) and $p$ (GPa): experimental (Ref. 23) and computed unit cell axis $a$, $b$, $c$ (Å), angles $\alpha$, $\beta$, $\gamma$ (degrees) and volume $V$ ($\text{Å}^3$). The lattice is triclinic, space group $P\overline{1}$ ($C_{1i}$), with $Z = 1$.

| $T$ | $p$ | $a$  | $b$  | $c$  | $\alpha$ | $\beta$ | $\gamma$ | $V$  | $G(p,T)$ |
|-----|-----|------|------|------|-----------|---------|----------|------|----------|
| 4.5 | 0   | 6.519| 8.920| 15.052| 95.32     | 96.09   | 110.44   | 807.6| 229.034  |
|     |     | calc.| 6.571| 9.147| 15.073   | 93.94   | 95.07    | 111.85| 832.6    | -229.056 |
| 20  | 0   | 6.543| 8.968| 15.114| 95.34     | 96.05   | 110.30   | 819.1| -229.056 |
|     |     | calc.| 6.571| 9.147| 15.074   | 93.94   | 95.07    | 111.85| 832.6    | -229.056 |
| 120 | 0   | 6.561| 9.013| 15.173| 95.07     | 95.93   | 110.28   | 829.2| -231.677 |
|     |     | calc.| 6.577| 9.159| 15.095   | 93.85   | 95.07    | 111.82| 835.9    | -231.677 |
| 298 | 0   | 6.615| 9.100| 15.286| 94.38     | 95.59   | 109.78   | 855.9| -242.678 |
|     |     | calc.| 6.591| 9.189| 15.145   | 93.64   | 95.08    | 111.72| 844.2    | -242.678 |
| 4.5 | 1.5 | 6.449| 8.986| 15.034| 94.79     | 96.57   | 111.29   | 799.1| -211.930 |
|     |     | calc.| 6.556| 9.117| 15.048   | 94.05   | 95.14    | 111.85| 826.1    | -211.930 |
| 6.1 | 4.6 | 6.433| 8.947| 14.927| 95.15     | 96.77   | 111.40   | 786.1| -175.319 |
|     |     | calc.| 6.532| 9.069| 15.007   | 94.20   | 95.27    | 111.86| 816.0    | -175.319 |

TABLE III. Low energy $A_u$ phonons of $\beta$-(BEDT-TTF)$_2$I$_3$.

| Expt. | Calc. | $\nu_1$ | Approximate description | BEDT-TTF$^+_{2}$ (%) |
|-------|-------|---------|-------------------------|---------------------|
| cm$^{-1}$ | cm$^{-1}$ | I$_3$ (%) | lattice | internal | I$_3$ (%) | lattice | internal |
| 216   |       | 98      | 98                      | 90                  |
| 173   |       | 90      | 90                      | 88                  |
| 151   |       | 26      | 26                      | 86                  |
| 133   |       | 8       | 8                       | 86                  |
| 130   |       | 8       | 8                       | 86                  |
| 124   |       | 48      | 48                      | 86                  |
| 114   |       | 8       | 8                       | 86                  |
| 95    |       | 24      | 24                      | 72                  |
| 91    |       | 56      | 56                      | 40                  |
| 84    |       | 13      | 13                      | 34                  |
| 74    |       | 56      | 56                      | 44                  |
| 71    |       | 26      | 26                      | 12                  |
| 69    |       | 22      | 22                      | 36                  |
| 67    |       | 8       | 8                       | 18                  |
| 62    |       | 40      | 40                      | 36                  |
| 57    |       | 22      | 22                      | 20                  |
| 55    |       | 23      | 23                      | 28                  |
| 43    |       | 11      | 11                      | 26                  |
| 33    |       | 44      | 44                      | 30                  |
| 17    |       | 41      | 41                      | 36                  |

$^a$From Ref. 22
TABLE IV. Low energy $A_g$ phonons and coupling constants of $\beta$-(BEDT-TTF)$_2$I$_3$.

| Expt. $^a$ cm$^{-1}$ | Calc. cm$^{-1}$ | $I_3$ (%) | BEDT-TTF$_2$ (%) | Approximate description | Coupling Constants (meV) $^b$ | $\epsilon_j$, meV |
|----------------------|----------------|------------|------------------|-----------------------|----------------------------|----------------|
|                     |                | lattice    | internal         | $g(AB; j)$            | $g(AC; j)$                | $g(AE; j)$       | $g(AH; j)$       |
| 214                 | 207            | 90         |                  | −1                    | −1                         |                |                |
| 179                 | 172            | 92         |                  | −1                    | −1                         |                |                |
| 165                 | 16             | 84         |                  | 3                     | 2                          | −1             |                |
| 149                 | 144            | 16         | 80               | −1                    | 2                          | 1              | −2             |
| 131                 | 12             | 86         |                  | −6                    |                            |                |                |
| 121                 | 120            | 89         |                  | −3                    | 1                          | 1              | −1             |
| 113                 | 58             | 32         |                  | −13                   | 7                          | 3              | −1             |
| 111                 |                | 90         |                  | −4                    | 1                          | −1             | 3              |
| 91                  | 87             | 10         | 50               | 2                     |                            |                |                |
| 81                  | 48             | 48         |                  | −1                    | −1                         | −1             | −5             |
| 73                  | 8              | 88         |                  | 2                     |                            |                |                |
| 64                  | 78             | 22         |                  | −4                    | 6                          | −3             | 3              |
| 60                  | 18             | 50         |                  | 1                     | −3                         | −4             | 5              |
| 53                  | 51             | 25         | 50               | 4                     |                            | −6             | 3              |
| 49                  | 20             | 66         | 14               | 4                     | −3                         | −1             | 2              |
| 39                  | 44             | 33         |                  | −1                    | −2                         | −2             | 2              |
| 32                  | 32             | 56         | 16               | 6                     | −2                         | −5             | 1              |
| 27                  | 29             | 10         | 76               | −4                    | 4                          | 2              | 2              |

$a$From Ref. 643.

$b$The modulated hopping integrals between dimers are labeled according to Ref. 22; the calculated equilibrium values are: $t_{AB} = 0.22$ eV, $t_{AC} = 0.08$ eV, $t_{AE} = 0.10$ eV, $t_{AH} = 0.06$ eV.
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FIG. 1. Calculated and experimental of β-(BEDT-TTF)$_3$I$_3$ crystallographics axis lengths as functions of temperature and pressure. The experimental points are taken from Ref. 23 (diamonds) and from Refs. 24, 25 (asterisks).
FIG. 2. Specific heat of $\beta$-(BEDT-TTF)$_2$I$_3$ as a function of $T$. The dots represent the experimental $C_p$, from Ref. [39]. The dotted line represents computed $C_V$ due to lattice modes only in the RMA approximation, whereas the dotted line is the $C_V$ obtained from coupled lattice and intra-molecular modes.

FIG. 3. Dispersion curves and density of states $F(\omega)$ of $\beta$-(BEDT-TTF)$_2$I$_3$ low-frequency phonons. The zone edges are labeled according to Ref. [22].
FIG. 4. Upper panel: the Eliashberg function as measured from point–contact tunneling experiments (adapted from Ref. 46). Lower panel: the calculated contribution to $\alpha^2(\omega)F(\omega)$ from low frequency $e$-$lph$ coupled phonons.