PHYSICAL REVIEW B VOLUME 37, NUMBER 10 1 APRIL 1988

X-ray study of the incommensurate modulation of the organic superconductor β-di[bis(ethylenedithio)tetrathiafulvalene] tri-iodide

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(Received 18 September 1987)

An ambient-pressure x-ray study of the incommensurate phase of the organic superconductor β-di[bis(ethylenedithio)tetrathiafulvalene] tri-iodide, β-(BEDT-TTF)$_2$I$_3$ is presented. This phase appears at $T_c = 175$ K (a temperature which is lower than that previously reported, ~ 200 K), and is announced by quasi-isotropic structural fluctuations which have been followed until room temperature. Below T_c the incommensurate modulation is characterized not only by first-order satellite reflections, but also by higher-order satellites up to the fifth. Upon irradiation the temperature dependence of the first-order satellite intensity shows an anomalous decrease below about ~ 125 K, which has been interpreted as due to the formation of unmodulated regions in the vicinity of irradiation defects. These results provide a clue for the understanding of the phase diagram of β-(BEDT-TTF)$_2$I$_3$ under pressure and of anomalies observed at ambient pressure in the low-temperature electrical conductivity of cycled or irradiated samples.

I. INTRODUCTION

β-di[bis(ethylenedithio)tetrathiafulvalene] tri-iodide [β-(BEDT-TTF)$_2$I$_3$] is known as the first sulfur-based organic conductor to present superconductivity at ambient pressure (state β_L with $T_s \sim 1.5$ K).[1,2] A high-T_s state, named β_H, with $T_s \sim 7.4$ K, can be obtained under a relatively low pressure.[3-5] This state is preserved after depressurization at low temperature and superconductivity is observed below $T_s = 8.1$ K, provided the crystal is not heated above about 125 K.[6] The different behavior of the β_H and β_L states seems to be related to the existence of a structural modulation which is the object of the present study.

In the triclinic $P\bar{1}$ crystal structure of β-(BEDT-TTF)$_2$I$_3$, the nearly planar BEDT-TTF molecules form chains in the **a**+**b** direction which are packed in sheets in (**a**,**b**) planes. These sheets alternate with tri-iodide anion planes along **c**.[7-9] At room temperature and ambient pressure, the terminal ethylene groups of the BEDT-TTF molecules which are in close contact with I_3^- ions are disordered, with two nonequivalent orientations referred to as A and B.[7] Upon cooling at T_c (175–200 K, depending on the authors—see below), the compound undergoes a structural phase transition leading to an incommensurate modulation of the lattice.[10] The modulation has been studied from a collection of fundamental and first-order satellite reflection data at about 125 K. The analysis resulted in sinusoidal displacement waves of the tri-iodide anions (along **a**) and BEDT-TTF (ET) molecules (along **a**−**b**) with amplitudes of $U_{\mathrm{I}_3} = 0.27$ Å and $U_{\mathrm{ET}} = 0.11$ Å, respectively.[11]

The purpose of the present paper is to report a detailed structural study of the incommensurate modulation of β-(BEDT-TTF)$_2$I$_3$ at ambient pressure. Experimental conditions are given in Sec. II. The study of pretransitional fluctuations above T_c is presented in Sec. III and, below T_c, that, of the incommensurate modulation and its harmonics is the object of Sec. IV. During the study itself we observed important effects of the x-ray irradiation on the satellite intensity. These effects are described in Sec. V and related to the defect concentration. Finally a general discussion of the phase diagram of β-(BEDT-TTF)$_2$I$_3$ and its unusual behavior under pressure is given in Sec. VI.

II. EXPERIMENT

Our measurements were performed with seven crystals from different batches. They were prepared as usual by electrocrystallization. Five of them (one being 98% deuterated) were grown in Heidelberg. They were used for a first photographic survey of the structural phase transition and preliminary results were reported in Ref. 12. The other two crystals ($2 \times 2 \times 0.2$ mm^3), hereafter denoted 1 and 2, were prepared in Orsay. They were used for the diffractometric study which is the main object of this paper. However, it is worth pointing out that all the crystals (protonated or deuterated) gave the same value of T_c ($\simeq 175$ K) and the same incommensurate wave vector of modulation down to 12 K.

In the diffractometric study the crystals were attached to the cold stage of a closed-cycle helium cryocooler installed on a normal beam lifting-detector-type x-ray diffractometer. Monochromatized Cu $K\alpha$ radiation from a 12 kW rotating anode generator was employed. The samples were studied from 270 to 12 K.

Because of the irradiation damage produced by the x-ray photons the samples were exposed to the beam only during the strict time needed for the measurements. The irradiation dose received by the samples in the 12 kW rotating anode beam is estimated at about 220 Mrads/day of exposure. This value is derived from a previous determination performed on similar organic materials with the same experimental set up (27 Mrads/day), but with an x-ray source less powerful by a factor of 8.[13] In β-(BEDT-TTF)$_2$I$_3$ low-temperature ESR measurements[14] have shown that 4000 Mrads create 1% of localized spins per mole of ET (hereafter referred to as mol % of defects). Using these data, we are able to estimate the defect concentration of each sample from the knowledge of its irradiation time.

III. PRETRANSITIONAL FLUCTUATIONS

The diffuse scattering which announces the incommensurate modulation has been measured on sample 1 between room temperature and T_c. It appears in the form of slightly anisotropic and broad diffuse spots centered at the position of first-order satellite reflections, $\mathbf{q}_c$ (there is no sizeable diffuse scattering above T_c at the position of second-order satellite reflections—see Sec. IV). More quantitatively, we have measured as a function of temperature the peak intensity of the diffuse scattering above the background and its half width at half maximum (HWHM) along the a^*, b^*, and c^* directions (the setting which is used corresponds to the unit cell defined in Ref. 7).

In the vicinity of a structural phase transition and in the classical approximation, the q-dependent intensity of the critical scattering which develops above the background is proportional to[15]

$$I(\mathbf{q}) \alpha k_B T \chi(\mathbf{q}) \,, \tag{1}$$

where the generalized susceptibility $\chi(\mathbf{q})$ has generally a Lorentzian shape in the vicinity of $\mathbf{q}_c$:

$$\chi(\mathbf{q}) = \frac{\chi(\mathbf{q}_c)}{1+\delta\mathbf{q}\bar{\bar{\xi}}^2\delta\mathbf{q}} \,, \tag{2}$$

In (2), $\delta\mathbf{q}=\mathbf{q}-\mathbf{q}_c$ and $\bar{\bar{\xi}}^2$ is the 3×3 matrix of the square of correlation lengths, whose elements are obtained by the measurements of the HWHM of the critical scattering in various reciprocal directions.

Figure 1 gives the temperature dependence of $T/I(q_c)$, where $I(q_c)$ has been measured at $(\bar{3},1,0)-\mathbf{q}_c$. With a good approximation this quantity behaves like $T-T_c$, which corresponds to a Curie-Weiss behavior for $\chi(q_c)$ defined in (1). The linear extrapolation to zero gives a critical temperature $T_c=175$ K for the second-order structural phase transition of β-(BEDT-TTF)$_2$I$_3$.

Figure 2 gives the temperature dependence of ξ^{-1} along the a^*, b^*, and c^* directions. ξ^{-1} has been obtained from the HWHM of the profile of the diffuse scattering in the corresponding direction, corrected by the Gaussian experimental resolution (Voigt profile correction[16]). The experimental resolution used ($\delta Q_{a^*}=0.03$ Å^{-1}, $\delta Q_{b^*}=0.07$ Å^{-1}, $\delta Q_{c^*}=0.05$ Å^{-1}) is the HWHM of the $(\bar{3},1,0)-\mathbf{q}_c$ satellite reflections coming from the "condensation" of the diffuse scattering below T_c.

As expected for a second-order phase transition, ξ^{-1} vanishes (ξ diverges) at T_c. The value of T_c obtained in Fig. 2 is in good agreement with that of the linear extrapolation of $\chi^{-1}(q_c)$ (Fig. 1).

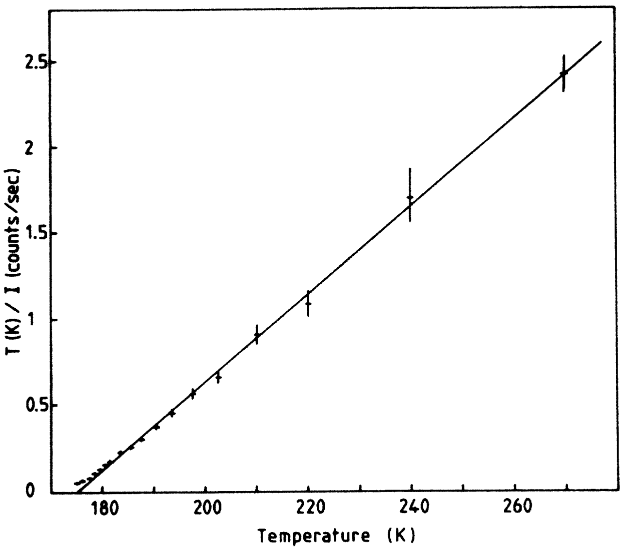

FIG. 1. Inverse of the peak intensity above the background I corrected by the thermal population factor T measured at $\mathbf{Q}_{-1}=(\bar{3},1,0)-\mathbf{q}_c$ for sample 1. The solid line gives a fit of the temperature dependence of this quantity by the Curie-Weiss law $T-T_c$, with an intercept $T_c=175$ K.

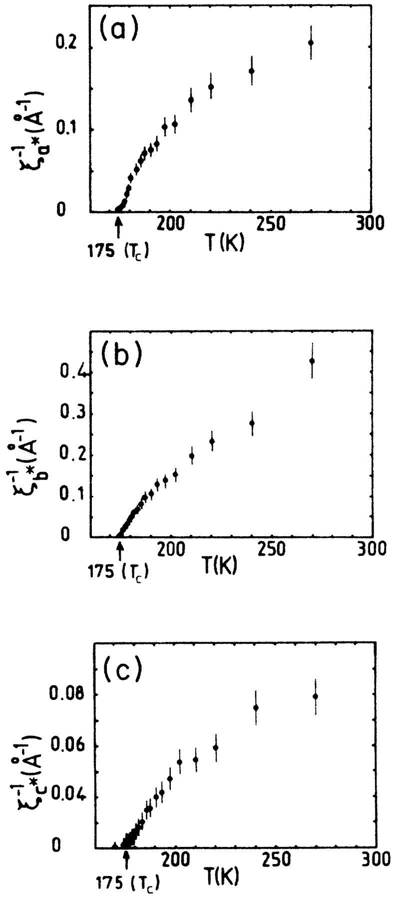

FIG. 2. Inverse correlation length of pretransitional fluctuations measured along a^*, b^* and c^*, as a function of the temperature. These quantities have been obtained after the resolution corrections described in the text.

Figure 2 shows, 2 or 3 K above T_c, a weak but visible rounding in the temperature dependence of ξ^{-1}. This unusual behavior could be caused by defects delaying the critical divergence of the correlation length when the average distance between them is comparable to ξ. In the present case, these defects are more likely due to x-ray damage of the sample. Their dose is estimated at 0.1 mol % for the data of this section.

Pretransitional fluctuations reveal that the incommensurate modulation of β-(BEDT-TTF)$_2$I$_3$ occurs after a second-order phase transition. Its critical temperature is $T_c = 175$ K at ambient pressure, a value somewhat lower than the ~ 200 K reported previously by Emge *et al.*[10] This T_c is consistent with that obtained in Sec. IV from the drop of first-order satellite reflection intensity. Independent structural studies performed on crystals belonging to different batches give also a T_c of 175 K.[12,17] It is also in agreement with reports of anomalies at 170–180 K in the temperature dependence of the paramagnetic susceptibility,[18] the transverse conductivity σ_{c^*},[19] and the lattice expansion along c^*.[20]

The incommensurate phase transition of β-(BEDT-TTF)$_2$I$_3$ is marked above T_c by strong fluctuations extending over a temperature range of about 100 K. The spatial fluctuations give rise to slightly anisotropic diffuse peaks with $\xi_{c^*}:\xi_{a^*}:\xi_{b^*} \simeq 6:3:2$. Typical values at 200 K are $\xi_{a^*} \sim 10$ Å, $\xi_{b^*} \sim 7$ Å, and $\xi_{c^*} \sim 20$ Å. From these numbers it appears that the spatial order is more correlated along c^*, i.e., a direction perpendicular to the (a,b) plane of ET molecules, where the electron gas has a two-dimensional (2D) character.[21] It follows that mechanisms, like the instability of the 2D Fermi surface, leading to the strongest correlations in the (a,b) plane can be discarded as driving forces of the structural phase transition of β-(BEDT-TTF)$_2$I$_3$. The strong coupling along c^* could be due to the short CH$_2$-I$_3$ distance which relates ET molecules and I$_3^-$ anions.

IV. SATELLITE REFLECTIONS

A. Experimental results

These measurements have been performed on weakly irradiated samples ($\sim 10^{-2}$ mol % defects). Below $T_c = 175$ K, first-order satellite reflections are easily detected. They are strong ($\sim \frac{1}{10}$ of the intensity of main reflections) and sharp (their width is limited by the instrumental resolution). They are located at $\mathbf{Q}_{\pm 1} = \mathbf{Q}_0 \pm \mathbf{q}_c$, where $\mathbf{Q}_0$ is a reciprocal vector of the average lattice and

$$\mathbf{q}_c = 0.075 \pm 0.003\mathbf{a}^* + 0.275 \pm 0.005\mathbf{b}^* + 0.205 \pm 0.005\mathbf{c}^*$$

Within the accuracy of our measurements we observed no variation of $\mathbf{q}_c$ in the temperature range 175–12 K. Our values of the $\mathbf{q}_c$ components are in good agreement with those of Leung *et al.*[11] measured at 125 K:

$$\mathbf{q}_c = 0.076(2)\mathbf{a}^* + 0.272(4)\mathbf{b}^* + 0.206(3)\mathbf{c}^* \ .$$

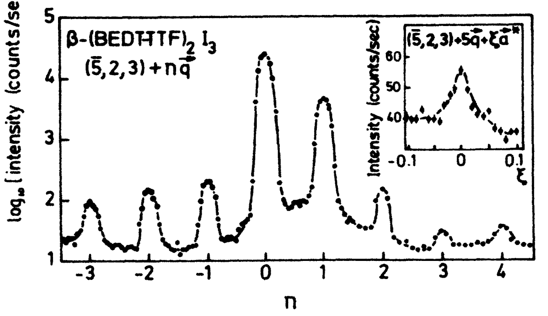

FIG. 3. Scan along the $\mathbf{q}_c$ direction of the Q_n reflections of sample 1 corresponding to $Q_0 = (\bar{5},2,3)$. Note that the intensity scale is in logarithmic units. The inset shows a scan in the $\mathbf{a}^*$ direction of the Q_5 satellite reflection.

Figure 3 shows a scan, from sample 1, in the $\mathbf{q}_c$ direction, originating from the $\mathbf{Q}_0 = (\bar{5},2,3)$ fundamental Bragg peak, which clearly reveals satellite peaks with $\mathbf{Q}_n = \mathbf{Q}_0 + n\mathbf{q}_c$ ($n = \pm 1, \pm 2, \pm 3, 4, 5$). All satellite reflections have the same width as that of fundamental ones, indicating long-range order.

The temperature dependence of the satellite reflections has been followed upon heating, except for the too-weak fifth-order satellites.

Figure 4 gives the temperature dependence of the $(\bar{3},1,0) - \mathbf{q}_c$ and $(\bar{6},3,3) + \mathbf{q}_c$ first-order satellite reflections of sample 2. The continuous growth of the first-order satellite reflection intensity (Fig. 4) shows also the second-order nature of the phase transition. Power-law fit of their temperature dependence is compatible with a $T_c \simeq 175$ K.

Figure 5 gives the temperature dependence of the second-, third-, and fourth-order satellite reflections of the $(\bar{4},1,\bar{1})$ fundamental reflection of sample 2. These satellite reflections appear progressively below T_c with no measurable precursors above T_c. Their intensity saturates abruptly below $T \sim 85$ K. Such a saturation of the intensity below about 85 K was also observed for other high-order satellite reflections like those originating from $\mathbf{Q}_0 = (\bar{5},2,3)$. It is also observed for some first-order satel-

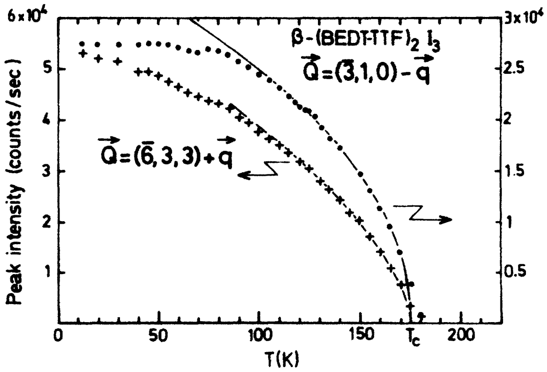

FIG. 4. Temperature dependence of the $(\bar{3},1,0) - \mathbf{q}_c$ and $(\bar{6},3,3) + \mathbf{q}_c$ satellite intensities of sample 2. The transition temperature $T_c = 175$ K has been determined by a power law fit in $(T_c - T)$ of the satellite intensity. The weak intensity measured above 175 K is due to critical scattering.

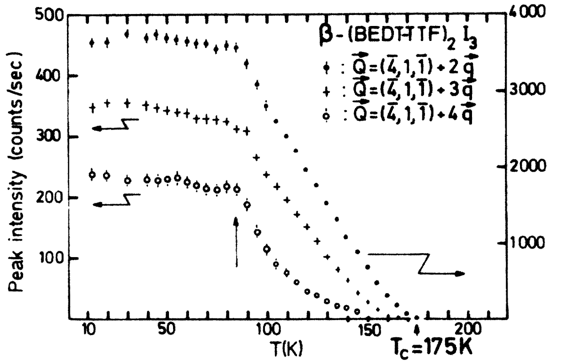

FIG. 5. Temperature dependence of the $(\bar{4},1,1)+2\mathbf{q}_c$, $+3\mathbf{q}_c$, $+4\mathbf{q}_c$ satellite intensities of sample 2 after background subtraction. The arrow indicates the temperatures below which the intensity remains roughly constant.

lite reflections like $(\bar{3},1,0)-\mathbf{q}_c$ (see Fig. 4).

Following the structural refinement of the incommensurate modulation performed by Leung *et al.*[11] at 125 K, the contribution of the ET and I$_3$ units to the satellite intensities shown in Figs. 4 and 5 can be obtained. It is found that $(\bar{6},3,3)+\mathbf{q}_c$ has a dominant contribution from the ET sublattice ($|F_{\mathrm{ET}}|/|F_{\mathrm{I}_3}|\sim 3$ where F_j is the structure factor of unit j) while $(\bar{3},1,0)-\mathbf{q}_c$ has a dominant contribution from the I$_3$ sublattice ($|F_{\mathrm{I}_3}|/|F_{\mathrm{ET}}|\sim 11$). This is also the case for the $(4,1,\bar{1})+n\mathbf{q}_c$ reflections ($|F_{\mathrm{I}_3}|/|F_{\mathrm{ET}}|>9$). Thus the saturation of the satellite intensity below 85 K is clearly observed for satellite reflections having a dominant contribution from the I$_3$ sublattice. It corresponds to a saturation of the amplitude of displacement of I$_3$ units (U_{I_3}). Apparently such a saturation is not observed for satellite reflections like $(\bar{6},3,3)+\mathbf{q}_c$ having a dominant contribution from the ET sublattice. The low-temperature behavior of the order parameters will be discussed in Sec. VI.

B. Analysis of the wave vector

The modulated structure associated with $\mathbf{q}_c$ is therefore incommensurate with the average lattice along the **a**, **b**, and **c** directions. This is a rather unusual feature, especially for a compound that exhibits some anisotropic properties and all the more so since we observe no temperature dependence of $\mathbf{q}_c$. This has not been explained so far. However, some properties of $\mathbf{q}_c$ and of the associated modulation are worth mentioning. Firstly $\mathbf{q}_c$ is normal to $\mathbf{a}-\mathbf{b}+\mathbf{c}$, $[\mathbf{q}_c\cdot(\mathbf{a}-\mathbf{b}+\mathbf{c})\simeq 0]$, with a good accuracy as the angle calculated from our $\mathbf{q}_c$ components is $(\mathbf{q}_c, \mathbf{a}-\mathbf{b}+\mathbf{c})=89.7°\pm0.8°$. It is also nearly perpendicular to the mean plane of the BEDT-TTF molecules (defined for instance by the four outer S atoms) as the corresponding angle is 85°±1°. Considering that the major component of the BEDT-TTF displacement is in the molecular plane and along $[1\bar{1}0]$, that is, nearly perpendicular to the long molecular axis, it corresponds approximately to a transverse polarization. Secondly, one can obtain the following relations:

$$\mathbf{q}_c\cdot(3\mathbf{a}+2\mathbf{b}+\mathbf{c})=1\ ,$$

$$\mathbf{q}_c\cdot(6\mathbf{a}+2\mathbf{b})=1\ ,$$

within experimental accuracy (the actual values are 0.98±0.03 and 1.0±0.03, respectively). It means that, for instance, BEDT-TTF molecules related by vectors like $3\mathbf{a}+2\mathbf{b}+\mathbf{c}$ or $6\mathbf{a}+2\mathbf{b}$ are in phase and it gives indications about the equiphase wave planes. Thus the $3\mathbf{a}+2\mathbf{b}+\mathbf{c}$ vector relates two different [110] stacks of molecules and in the $\mathbf{q}_c$ direction the wavelength $2\pi/q_c$ corresponds approximately to six molecules. Although we have no clear understanding of the origin of the triply incommensurate modulation, an important point is that the molecules are tilted with respect to the stacking axis while the wave vector of the modulation is almost normal to them. This induces complex couplings from stack to stack as reflected by the value of the $\mathbf{q}_c$ components which appear to be incommensurate. However, the three relations given above for the dot products with $\mathbf{q}_c$ form a system of three equations whose unknowns are the $\mathbf{q}_c$ components. The solution of this system gives a commensurate wave vector $q_c=\frac{1}{14}(\mathbf{a}^*+4\mathbf{b}^*+3\mathbf{c}^*)$. Consequently we estimate that although the modulation is probably truly incommensurate because of the mismatch between the observed components and $\frac{1}{14}$, $\frac{4}{14}$, and $\frac{3}{14}$ (Table I), it is actually very close to a commensurate description. It is therefore very surprising to observe no change of $\mathbf{q}_c$ with temperature, as one would expect a lock-in effect due to the potential of commensurability. However, the effect of this weak potential may be pertinent only at low temperature and we note that Schultz

TABLE I. Present data on the wave-vector components in the modulated phase of β-(BEDT-TTF)$_2$I$_3$.

	$T=120$ K[a]	$T=12$ K[b]	$T=4.5$ K[c]	Commensurate description[b]	$T=100$ K[d]
q_{a^*}	0.076(2)	0.075±0.003	0.074(1)	$\frac{1}{14}=0.0714$	0
q_{b^*}	0.272(4)	0.275±0.005	0.284(9)	$\frac{4}{14}=0.2857$	$\frac{1}{3}$
q_{c^*}	0.206(3)	0.205±0.005	0.212(7)	$\frac{3}{14}=0.2143$	$\frac{1}{3}$

[a] Leung *et al.* (Ref. 11).
[b] This work.
[c] Schultz *et al.* (Ref. 22).
[d] Endres *et al.* (Ref. 23).

et al.[22] by neutron diffraction at 4.5 K obtained $\mathbf{q}_c$ components compatible with the commensurate values (Table I). (We can therefore assume that a lock-in may occur at low temperature).

Obviously this should be substantiated by a detailed high-resolution study of the combined effects of pressure and temperature on the wave vector of the modulation.

Finally, we draw attention to the report by Endres *et al.*[23] of a $(0,\frac{1}{3},\frac{1}{3})$ superstructure to be present at 100 K. We have found no evidence for such an effect in the seven crystals that we examined. Unless the $(0,\frac{1}{3},\frac{1}{3})$ superstructure arises because of differences in the crystals (stoichiometry, presence of solvent), which are unlikely, a possible interpretation may be that because of a poor resolution (the authors mention a poor crystal quality at 100 K) the $\mathbf{q}_c$ components were approximated to $(0,\frac{1}{3},\frac{1}{3})$ during the data acquisition.

C. Analysis of the satellite intensities

The diffraction pattern from a sinusoidally modulated structure is composed of a infinite set of satellite reflections (for $\mathbf{q}_c$ incommensurate) centered at $\mathbf{Q}_n=\mathbf{Q}_o+n\mathbf{q}_c$ and of intensity[15]

$$I(\mathbf{K})=\sum_{n=-\infty}^{+\infty} |A^n(\mathbf{K})|^2 \sum_{|Q_0|} \delta(\mathbf{K}-n\mathbf{q}_c-\mathbf{Q}_o) . \qquad (3)$$

In the case of the modulation of $(\text{BEDT-TTF})_2\text{I}_3$, consisting mainly of translation of ET and I_3 rigid units,[11] the amplitude of the nth satellite reflection can be written under the form

$$A^n(\mathbf{K})=F_{\text{I}_3}(\mathbf{K})J_n(\mathbf{K}\cdot\mathbf{u}_{\text{I}_3})+F_{\text{ET}}(\mathbf{K})J_n(\mathbf{K}\cdot\mathbf{u}_{\text{ET}}) \times\exp[in(\varphi_{\text{ET}}-\varphi_{\text{I}_3})] , \qquad (4)$$

assuming a sinusoidal modulation in (3). $F_j(\mathbf{K})$, $\mathbf{u}_j$, and φ_j are respectively the structure factor, the amplitude and the phase of the modulation of the unit $j J_n(x)$ is the Bessel function of order n.

From the temperature dependence in the vicinity of T_c of the intensity of first-order satellite reflections, the critical exponent β of the order parameter $\eta(\alpha\,|\mathbf{u}_{\text{I}_3}|$ or $|\mathbf{u}_{\text{ET}}|\,)$ describing the modulation can be obtained according to $\eta\sim(T_c-T)^\beta$. Because of the large value of the scalar product $\mathbf{K}\cdot\mathbf{u}$ at satellite positions, the explicit variation $J_1(\mathbf{K}\cdot\mathbf{u})$ had to be used to extract β. From the fit of the intensity of four first-order satellite reflections dominated either by the ET or the I_3 structure factor, β is found to be 0.31 ± 0.03. Within experimental errors this value agrees with that expected $(\beta\sim\frac{1}{3})$ for an $(n=2, d=3)$ order parameter describing a single $\mathbf{q}$ incommensurate modulation.

Let us now consider the origin of high-order satellite reflections shown in Fig. 3. As a result of the development (3), such satellites can arise from harmonics of diffraction of a sinusoidal modulation. In that case, the intensity I_n of the nth satellite is just $|A^n(\mathbf{K})|^2$, where $A^n(\mathbf{K})$ given by (4) can be easily calculated with the atomic displacements obtained in the refinement performed at 125 K.[11] The calculation, performed for satellite reflections having a dominant contribution of the I_3 sublattice, like the $(\bar{4},1,\bar{1})+n\mathbf{q}_{c'}$ gives an intensity comparable to the experimental one for $n=2$ and $n=3$ but 20 times lower for $n=4$. An even larger difference is expected from the pure observation of the fifth-order satellite. This simple calculation shows that, at least for $n>3$, the observed satellite reflections are not due to diffraction harmonics of a sinusoidal modulation. The modulation thus appears as weakly anharmonic. The evaluation of its harmonic content is, however, very difficult to get, because the intensity of high-order satellite reflections is strongly affected by interferences between harmonics of modulation and harmonics of diffraction.

V. IRRADIATION EFFECTS

A. Experimental results

The $(\bar{6},3,3)+\mathbf{q}_c$ and $(\bar{4},1,\bar{1})+2\mathbf{q}_c$, $+3\mathbf{q}_c$, $+4\mathbf{q}_c$ satellite reflections, previously considered, were measured once again as a function of the temperature after about two days of irradiation, corresponding to the formation of about 10^{-1} mol % defects. As in Sec. IV, these four reflections were successively measured at each temperature. This allows to compare data which correspond to the same irradiation dose. At 12 K we have found that after two days of irradiation, the intensity of the $(\bar{6},3,3)+q_c$ satellite is reduced by 27%, and that of the $(\bar{4},1,\bar{1})+2\mathbf{q}_c$, $+3\mathbf{q}_c$, $+4\mathbf{q}_c$ satellites are reduced by 46%, 57%, and 75%, respectively. Thus the higher is the order of harmonic the larger is the intensity decrease. With this irradiation dose, the T_c obtained from the vanishing of the intensity of first-order satellite is not drastically reduced (ΔT_c is less than 2 K for 0.1 mol % defects), nor is the temperature, ~85 K, below which a saturation of the intensity of the higher order satellites occurs.

The effects of irradiation on first-order satellite reflections have been more particularly followed on the $(\bar{3},1,0)\pm\mathbf{q}_c$ reflections of sample 1. Both satellite reflections behave similarly upon irradiation. Figure 6 shows the temperature dependence of the $(\bar{3},1,0)+\mathbf{q}_c$ reflection upon heating for about 10^{-1} mol % defects (curve 1). In addition to the saturation of the satellite intensity below 85 K, occuring whatever the irradiation dose, a weak anomaly appears around 125 K under the form of a change of slope. Figure 6 shows that the decrease of intensity, from curve 1 to curve 2, which results from the further addition of about 10^{-1} mol % defects in the sample, is not uniform in the whole temperature range. The most drastic reduction occurs at low temperature. It leads to the formation of a broad maximum at about 125 K in the temperature dependence of the $(\bar{3},1,0)\pm\mathbf{q}_c$ reflections.

Effects of thermal cycling and of cooling rate have also been observed on the sample with $\sim2.10^{-1}$ mol % defects. The temperature dependence of the $(\bar{3},1,0)+\mathbf{q}_c$ reflection plotted on curves 2 and 3 shows the difference of behavior upon slow cooling (~5 min of measuring time per data point) and upon heating two times as fast. Similar measurements are shown on curves 4 and 5 where

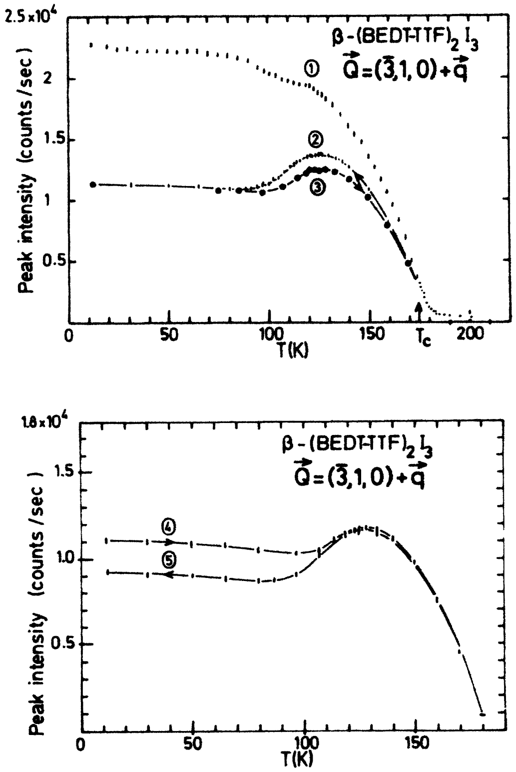

FIG. 6. Temperature dependence of the $(\bar{3},1,0)+\mathbf{q}_c$ satellite reflection of sample 1 with defects concentration of about 10^{-1} mol % defect (curve 1) and 2.10^{-1} mol % defects (curves 2,3,4,5). Curves 1, 3, and 4 have been taken upon heating and curves 2 and 5 upon cooling. Between curves 3 and 4 the sample has been quenched from T_c to 12 K at a speed of ~ 3 K/min. During the measurements the sample stays at each temperature during about 5 min. The decrease of intensity at 12 K between curves 3 and 5 is due to irradiation of the sample during 3 cycles.

the intensities were just recorded upon heating after a rapid cooling (~ 3 K/min), then upon slow cooling. The results of the first cycle indicate that the intensity saturates at ~ 85 K and that kinetic effects occur between 85 and 175 K. The results of the second cycle confirm that the value of the low-temperature intensity depends on the cooling rate and that the system stays frozen below 85 K. In both cycles, the maximum at ~ 125 K remains. We emphasize that the main effect of a rapid cooling is not to decrease the low-temperature satellite intensity but to increase it.

Finally, let us mention that at the scale of our resolution, given in Sec. III, we have not observed a significant broadening of the satellite reflections for defect concentrations up to 2×10^{-1} mol %, and that the wave vector of the incommensurate modulation has not changed in a measurable way.

B. Analysis of the incommensurate modulation in the presence of irradiation defects

Previous studies have dealt with the effects of irradiation in low-dimensional conductors and especially 1D organic conductors.[24] In our case, the defects probably consist of alterations of the ET molecules such as broken bonds or chemical rearrangements of the molecule, although no information on the chemical species produced is available. It has been shown[25] that the molecular displacements associated with irradiation defects induce local strains in the average structure. In the case of β-(BEDT-TTF)$_2$I$_3$, it has been previously noted[11] that iodine interacts strongly with the ethylene groups of the ET molecule via CH$_2$-I$_3$ contacts. In particular, a shift of the neighboring I$_3$ molecule is required for the occupancy of configuration *B* of the terminal ethylene groups in order to avoid an unfavorably short CH$_2$-I$_3$ contact distance. Through the modulation of CH$_2$-I$_3$ contact distance, local deformations of the ET and I$_3$ sublattices will certainly influence the occupations of configurations *A* and *B* of the ET molecules. Leung *et al.*[11] have suggested that the ethylene-anion interaction might be the driving force of the incommensurate phase transition and that the ethylene groups order significantly below T_c in the *A* or *B* configurations according to an occupational modulation of wave vector $\mathbf{q}_c$. In this picture, the incommensurate modulation should be drastically modified by irradiation defects.

The irradiation defects have however a less drastic effect on the incommensurate modulation of β-(BEDT-TTF)$_2$I$_3$ than on the structural phase transition of 1D conductors like the anion-ordering (AO) transition of (TMTSF)$_2$ClO$_4$ (Ref. 13) or the charge density wave (CDW) transition of TMTSF-DMTCNQ.[26] The satellite intensity of the incommensurate modulation of β-(BEDT-TTF)$_2$I$_3$ decreases by a factor of 2 with about 1.5×10^{-1} mol % of defects, while the intensity of the $(0,\frac{1}{2},0)$ reflections of (TMTSF)$_2$ is reduced by the same amount with only 0.18×10^{-1} mol % of defects.[13] The shift of the critical temperature of the incommensurate modulation of β-(BEDT-TTF)$_2$I$_3$ is less than -20 K/mol % defects while the critical temperature of the AO of (TMTSF)$_2$ (of 24 K) is depressed with a rate of -35 K/mol %,[13] and that of the CDW ordering of TMTSF-DMTCNQ (of 42 K) decreases with a rate of -110 K/mol %.[27] It appears clearly that the phase transition of β-(BEDT-TTF)$_2$I$_3$ is less sensitive to irradiation damages than that of TMTSF-DMTCNQ or (TMTSF)$_2$. In TMTSF-DMTCNQ the defects pin the CDW in a large volume through the response of the 1D electron gas.[26] In (TMTSF)$_2$, the defects easily disorder the anions, which are weakly coupled together and with the organic stacks.[13] In β-(BEDT-TTF)$_2$I$_3$ the electron gas is believed to be 2D (instead of 1D in TMTSF-DMTCNQ), and is probably only weakly involved in the incommensurate modulation as shown by the study of pretransitional fluctuations (Sec. III) and the observation of only very weak anomalies at T_c in electronic properties.[18,19] Compared to (TMTSF)$_2$ the coupling between the anions is certainly much stronger. According to Leung *et al.*[11] the I$_3^-$ are also coupled to the ethylene groups of the organic stack. This coupling involves hydrogen bonds which are certainly strongly disturbed by irradiation damage. It is thus surprising that if, as assumed in Ref. 11, the driving force of the phase transition of β-(BEDT-TTF)$_2$I$_3$ lies mainly on this interaction, the damages affect so weakly the critical temperature and the wave vector of the incommensurate modulation.

The strong decrease of satellite intensity observed upon irradiation without a drastic change of T_c means that defects created have only a *local effect* on the order parameter η of the incommensurate modulation. Let us take first a crude picture where the defects kill locally the modulation. The sample will thus be composed of regions not modulated in an unperturbed matrix. In that case, the decrease of intensity will be proportional to the volume of the nonmodulated regions, and will be the same for all the satellites, whatever their order of reflection. Such a situation is not observed (see Sec. V A). This suggests that there is a certain continuity in the modulation wave from non perturbed to perturbed regions, with only a perturbation of the amplitude and phase of the local order parameter by the local strains associated to irradiation defects. Such a wave is schematically represented by Fig. 7. In that case, assuming a long-range modulation, which is compatible with the nonbroadening of satellite reflections, the decrease of the satellite intensity can be accounted for by an increase of the Debye-Waller factor due to an increase of the mean-square fluctuation of the order parameter (or more likely to that of $\langle \delta\eta^2 \rangle$, where $\delta\eta=\eta-\langle \eta \rangle$ is the local fluctuation of the order parameter from its average value $\langle \eta \rangle$). Clearly $\langle \delta\eta^2 \rangle$ increases with the irradiation dose, leading to an overall decrease of the satellite intensity. However this simple picture can explain neither the cusp observed around 125 K in the temperature dependence of first-order satellite reflection for low irradiation doses nor its change into a maximum of intensity for higher doses (Fig. 6). In the same formulation, one has to invoke an anomalous increase of $\langle \delta\eta^2 \rangle$ below 125 K. This behavior cannot be due to the accumulation of defects during the measurements, because it is reversible in temperature. It does not reflect the expected behavior of the Debye-Waller factor upon cooling, which usually decreases for decreasing temperatures as usually does $\langle \delta\eta^2 \rangle$ for a normal order parameter. It indicates some unusual behavior of the order parameter, that we shall rely in the next section with a change around 125 K in the dependence of the free energy with η.

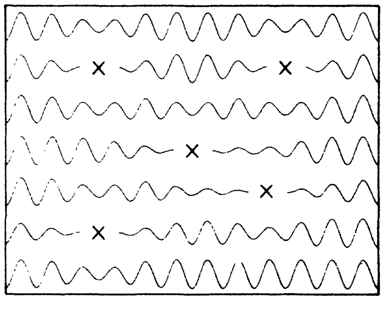

FIG. 7. Schematical representation of the modulation wave in presence of localized defects, increasing locally, by the associated strain field, the mean-square fluctuation of the order parameter.

VI. THE PHASE DIAGRAM OF β-(BEDT-TTF)$_2$I$_3$

β-(BEDT-TTF)$_2$I$_3$ shows a very subtle and not understood interplay between the presence of an incommensurate modulated structure and two superconducting states having quite different T_s. The low T_s state occurs in the presence of the incommensurate state (β_L phase) while the high T_s state, usually obtained above a critical pressure ($P_c \sim 350$ bars),[28–30] is achieved when the structure is nonmodulated (β_H phase).[22] The anomalous feature of the phase diagram of β-(BEDT-TTF)$_2$I$_3$ is that the β_H state can be preserved at ambient pressure if the sample is depressurized at low temperature, and if the sample is not heated above about 125–130 K.[6,19,30] Conversely, the β_L state can be kept above P_c if the sample is not heated above about 100 K.[30,31] This means that the β_L and β_H states have large domains of metastability as a function of temperature and pressure. These features can be understood by the development of secondary minima in the free energy being able to keep the β_L or β_H state in metastable equilibrium. The pressure and temperature dependence of the coefficients of a Landau expansion of the free energy as a function of η, able to mimic the required shape of the free energy, has been derived recently.[30] This free energy has been calculated recently[32] on a microscopic basis, taking especially into account the two configurations *A* and *B* of the ethylene groups. These theoretical considerations have explained the tricritical point experimentally observed at P_c.[30] In this work only the variation of the free energy with η, is required to interpret the structural results as a function of the temperature at ambient pressure. Figure 8 gives the η dependence of the free energy deduced from Ref. 32. Below T_c (second-order phase transition to the β_L phase) the free energy, F, develops two minima at $\pm\langle \eta \rangle$, the average amplitude of the incommensurate modulation. The nonmodulated state, $\eta=0$, is an extremum for F. Below T_m a secondary minimum appears for $\eta=0$. It corresponds to the nonmodulated metastable state (β_H phase) in which the system is trapped by depressurization at temperatures lower than about T_m. Usually the secondary minimum does not lead to thermodynamics anomalies at T_m if, by thermal fluctuations, the system explores only the values of the free energy where η is close to $\pm\langle \eta \rangle$. This is the case of homogeneously modulated samples. Now let us consider an inhomogeneously modulated sample where, because of local strains, for example, η can fluctuate on a large scale. These fluctuations could even reach the vicinity of $\eta=0$ for a large number or strong sources of strains (a situation shown by the oblique lines of Fig. 8). In this case, the system can gain some free energy below T_m by reducing the amplitude of modulation in the region where the order parameter has values close to zero. This process, which nucleates locally the phase β_H, will thus reduce the rate of increase of the satellite intensity or even reduce its intensity if there is a sizeable volume of the sample occupied by the β_H phase. It provides the simplest explanation for the well-defined anomaly observed at 125 K in the temperature dependence of satellite intensities. In agreement with this explanation, the temperature at which this anomaly occurs is precisely

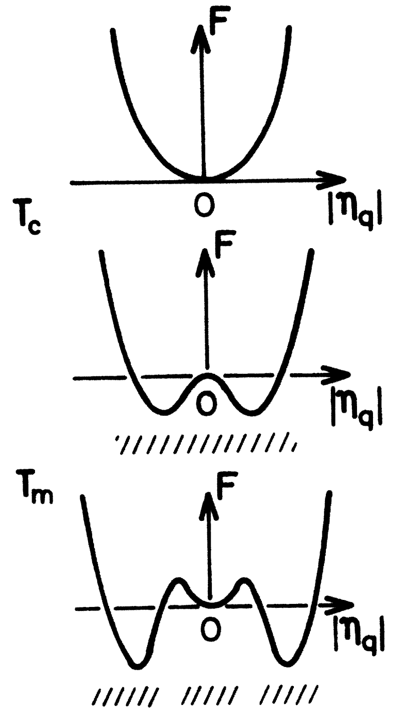

FIG. 8. η ($\equiv \eta_{q_c}$) dependence of the free energy (F) in the three temperature ranges delimited by T_c and T_m defined in the text. The oblique lines indicate schematically the range of values of η explored in an irradiated sample.

that found for the limit of stability of the β_H state in samples depressurized at low temperature.[6,19,30] In this picture one obtains the paradoxical results that irradiation defects induce locally the β_H state, which has a higher T_S than the underlying phase β_L. Anomalies observed around 6–7 K in the conductivity of irradiated samples[14,33] are probably the signature of a local superconductivity of higher T_s in the nonmodulated and strained parts of the sample. This mechanism can also explain the origin of similar anomalies observed at room pressure in samples probably strained by thermal cycling[21,34] or by depressurization at ambient temperatures.[35]

The ordering of ethylene groups between the A and B configurations and the ethylene-iodine interaction are probably the clue for the explanation of the unusual features of the phase diagram of β-(BEDT-TTF)$_2$I$_3$. The peculiarity of the β(BEDT-TTF)$_2$I$_3$ structure is that iodine interacts strongly with the ethylene groups of the ET molecule via CH$_2$-I$_3$ contacts, with, however, enough flexibility to allow (at least in ambient conditions) the occupancy of the energetically least-favorable B configuration.[11] In that case, a shift of the neighboring I$_3$ molecule is required for the occupancy of configuration B in order to avoid an unfavorably short CH$_2$-I$_3$ contact distance. However, there is evidence that the ethylene group configurations A and B, which are disordered at room temperature and ambient pressure, order in the favorable A configuration (where the H-I distances are longer) either under pressure at room temperature[36] or at low temperature under a modest pressure.[22] At lower pressure, through the modulation of CH$_2$-I$_3$ contact distances, the incommensurate displasive distortion of the iodine sublattice certainly influences the occupation of configurations A and B; conversely the ordering of ethylene will fix more rigidly the iodine positions. If for kinetic reasons the occupancy of configurations A and B becomes frozen below a given temperature, it would result in a saturation in the rate of increase of the amplitude of distortion of the iodine sublattice, U_{I_3}. This provides the simplest explanation for the anomalous stop at 85 K in the rate of increase of the intensity of satellite reflections dominated by the I$_3$ sublattice (see Figs. 4 and 5). In close relation with these observations, we note that NMR data indicate that there is still a substantial ethylene motion above $\sim$100 K.[37] Upon irradiation one expects in addition to these kinetic effects (modified by the disorder changing locally the barrier potential between the configurations A and B of the ethylene groups) also kinetics for the local transformation between the β_L and β_H configurations. The latter effects have been clearly observed in Sec. V.

The ordering of ethylene groups among a discret set of A and B configurations implies a regular distribution of configurations A or B at low temperature and necessarily a nonsinusoidal modulation. Such a wave will give rise to harmonics of modulation. Only harmonics of weak amplitude of displacement are compatible with the experimental observation (see Sec. IV). However, the freezing of the occupancy wave of the ethylene groups below 85 K probably prevents the complete development of these harmonics at low temperatures.

VII. CONCLUSION

We have performed a structural study of the incommensurate phase transition of β-(BEDT-TTF)$_2$I$_3$ at ambient pressure. The critical temperature T_c was established from the temperature dependence of pretransitional fluctuations and first-order satellite reflections. At this temperature, $T_c \simeq 175$ K, only weak anomalies are observed in the physical properties of β-(BEDT-TTF)$_2$I$_3$. The structural phase transition has been characterized by the temperature dependence of the order parameter below T_c, the susceptibility associated with this order parameter, and the correlations lengths above T_c. The 2D electron gas of the organic sublattice is apparently not responsible for this phase transition. The ordering of the ethylene groups of the ET molecule between two A and B configurations is certainly involved in the incommensurate modulation. We have suggested that this ordering is responsible, through the kinetics associated with this ordering, for the saturation of the iodine order parameter below about 85 K. It is also probably at the origin of the harmonics of distortion observed up to the fifth order.

Upon irradiation an additional anomaly in the temperature dependence of the intensity of first-order satellite reflections is observed around 125 K. We have related this observation with the development of a second minimum in the free energy, in agreement with our present understanding of the phase diagram of β-(BEDT-TTF)$_2$I$_3$ under pressure. The stabilization of this minimum in strained volumes of β-(BEDT-TTF)$_2$I$_3$, leads to the local formation of the unmodulated phase β_H which shows superconductivity at higher values of T_s than the modulated phase β_L.

ACKNOWLEDGMENTS

We have benefited from useful interactions with P. A. Albouy, S. Bouffard F. Creuzet, G. Creuzet, L. Forro, J. Friedel, T. Garel, B. Hamzic, S. Kagoshima, W. Kang, S. Megtert, and L. Zuppiroli. We are especially indebted to D. Schweitzer for giving us the samples used in the preliminary studies of this work, and for fruitful discussions. The Laboratoire de Physique des Solides, Université Paris-Sud is "Laboratoire associé au Centre National de la Recherche Scientifique No. 2."

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