PHYSICAL REVIEW B VOLUME 51, NUMBER 21 1 JUNE 1995-I

X-ray-scattering study of the metal-phthalocyanine-iodine quasi-one-dimensional molecular conductors

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(Received 26 October 1994; revised manuscript received 30 January 1995)

X-ray-scattering measurements on several newly synthesized, high-purity metal-phthalocyanine-iodine quasi-one-dimensional conductors reveal that, in contrast to previous materials, the iodine sublattice is ordered at all temperatures. The crystal symmetry is thus modified from tetragonal $P4/mcc$ to monoclinic $P2/c$ with a supercell unit volume three times larger. This new symmetry, which does not modify the dispersion of the one-dimensional band structure in the vicinity of the Fermi level, is consistent with the metallic behavior of the M(pc)I family. However, a metal-insulator transition could be induced if the c glide-plane symmetry of $P2/c$ is broken due to the stabilization of a $2k_F$ density-wave ground state.

In recent years low-dimensional molecular metals have been the object of considerable interest because of their tendency to exhibit original phenomena causing these materials to become insulators;[1,2] the electron-phonon coupling driven Peierls instability, the spin-density-wave formation, and the anion ordering transition represent significant examples of such phenomena. In these low-dimensional conductors special attention has been devoted to the series of metalphthalocyanine-iodine M(pc) I, (M=Cu, Ni, and Co), whose physical properties exhibit highly one-dimensional (1D) features down to low temperatures.[3–6] For the Ni and Cu compounds the positive sign of the thermoelectric power suggests that the conducting path is realized through π-π interactions of the phthalocyanine stacks, while the charge of Ni^{2+} and Cu^{2+} remains constant. In the first synthesis Ni(pc)I showed a conductivity peak at about 20–30 K with a drop to lower temperatures suggesting the occurrence of a Peierls instability.[4] In Cu(pc)I a one-dimensional Kondo lattice is formed at low temperatures due to the interaction of the d-electron localized spins ($S=\frac{1}{2}$) on the Cu^{2+} with the π conduction electrons.[7] The thermopower is negative for Co(pc)I and the conducting path is rather along the d_z^2 orbitals of the Co whose oxidation state is $\mathrm{Co}^{(7/3)+}$. This compound and some Co/Ni alloys are the only ones of the series to exhibit a metal-insulator-like transition below 100 K.[8]

Because of these features M(pc)I crystals can be understood as one-dimensional (1D) metals with or without coupling to d-electron spins along the conducting path. However, crucial issues are still incompletely resolved, such as the role of the metal ion, the anisotropy of the conductivity, and the intrinsic transport properties in the absence of disorder. When the metal ion M is replaced by the simplest chemical functionality of two hydrogen atoms, H_2(pc)I shows a metallic conductivity very similar to that of the parent compound Ni(pc)I.[5] It has been shown recently that when their conductivity is not limited by impurities H_2(pc)I and Ni(pc)I remain metallic down to 3 K with an absolute value of the conductivity 30-fold greater than the room-temperature value.[9] This behavior is now believed to represent the intrinsic charge transport properties of these materials at low temperatures. Below 3 K the conductivity decreases weakly as T^2 and saturates at a high value.[10] The conductivity maximum at about 3 K is slightly depressed by a magnetic field. Such features are not clearly explained, but they could be related to the onset of a charge-density-wave (CDW) or of a spin-density-wave (SDW) instability. Following the improvement in crystal quality Murata an coworkers[11] investigated the electronic properties of Ni(pc)I at low temperatures under pressure. In contrast to the ambient pressure data, a low-temperature insulating behavior was clearly stabilized under modest pressures of few kbar. The metallic properties are, however, recovered at higher pressure without any evidence of superconductivity. However, the boundary of the temperature-pressure phase diagram was found to depend strongly on the batch of samples investigated [compare Refs. 11(a) and 11(b)]. This suggests that disorder has a crucial influence on the low-temperature physical properties and the instabilities of the M(pc)I series.

The structure, which is the same for all compounds including their alloys,[12,13] consists of metal-over-metal stacks of partially oxidized $M(\mathrm{pc})^{0.33+}$ groups surrounded by linear chains of triodide anions I_3^-. The Ni(pc)I structure was analyzed in detail by Schramm *et al.*[12] The columnar stacks are made of two equidistant M(pc)

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molecules staggered by about 40°, well separated from iodine chains located in channels defined by the benzo groups of the nearby phthalocyanine ligands. Both kinds of chains are running along the *c* direction. On the basis of a series of Weissenberg and precession photographs, the *M*(pc) sublattice (noted "or" below) and the average iodine sublattice were assigned to the Laue group 4/mmm of the tetragonal system. On the grounds of systematic absences of $(0kl)$ and (hhl) reflections with l_{or} odd and after refinement of the structure, this space group was identified as $D_{4h}^{2}-P4/mcc$ [l_{or} is the Miller index of the *M*(pc) sublattice of period c_{or}]. In addition to the normal Bragg scattering a diffuse scattering confined to planes perpendicular to the *c* axis, with an interplanar spacing of $\frac{2}{3}\,c_{\mathrm{or}}^{*}$, was observed. This indicated that in these samples iodine is relatively well ordered in channel direction and disordered between channels. The intrachannel iodine periodicity $c_{\mathrm{I}}=\frac{3}{2}c_{\mathrm{or}}$ of 9.7 Å is consistent with the formation of a I_3^- repeat unit. An illustration of the iodine disorder which explains the data is shown Fig. 1(a). In each channel, chains of ordered I_3^- entities can be formed by displacing two iodine atoms out of three by an amount $\pm d$ from an average lattice of period $c_{\mathrm{or}}/2$, the central iodine atom remaining fixed. As shown Fig. 1(a) there are three distinct ways to form I_3^- trimers from this average iodine lattice. They occur randomly in the structure, accounting for the observed interchannel disorder. However, the spatial average of the iodine position remains in commensurate relationship with the *M*(pc) sublattice which explains the absence of diffuse planes for $l_{\mathrm{I}}=3n$ (n integer), where l_{I} is the Miller index of the iodine chains of period c_{I}. This kind of disorder on a commensurate sublattice must be contrasted with that observed in other triodine organic conductors such as $\mathrm{TTT}_2\mathrm{I}_{3+\delta}$ or $\mathrm{DIPS}\phi_4(\mathrm{I}_3)_{0.76}$ where the I_3^- intrachain repeat periodicity is in incommensurate relationship with the host organic lattice periodicity.[14]

According to Murata *et al.*[11(a)] the CDW or SDW instability could be suppressed at ambient pressure by the broadening of the one-dimensional Fermi surface due to the iodine disorder. Under pressure the suppression of this disorder [due to the reduction of the mismatch between the pc-pc and I-I local distances according to Ref. 11(a)] could restore the density-wave metal-insulator transition. This nesting transition will be suppressed at a higher pressure by the warping of the Fermi surface due to the increase of the interstack coupling.

In order to test this explanation and to understand the physical properties of the materials of improved quality it is imperative to reexamine the crystal structure and its disorder. This is why we have undertaken an investigation of the x-ray diffraction from several crystals of the *M*(pc)I family at room temperature and at 20 K. No evidence of structural phase transition can be detected upon cooling, but our x-ray study reveals that the "known" crystal structure should be modified to take account of the ordering of the triodine sublattice at all temperatures. Possible implications of the modified structure on the electronic and transport properties will be discussed.

The *M*(pc)I crystals are grown in an H tube by the diffusion of solutions of iodine and *M*(pc) in either 1,2,4-trichlorobenzene or 1-chloronaphthalene. The synthesis of the *M*(pc) units is achieved by different methods which are partly described in Ref. 9. The growth technique yields generally to very thin needles (10–20 μm in diameter) of few mm long. We have chosen the biggest ones for the x-ray study in order to minimize the time exposure. The five crystals used had the following compositions covering an interesting range: $\mathrm{Cu}_{0.05}\mathrm{Ni}_{0.95}(\mathrm{pc})\mathrm{I}$, $\mathrm{Cu}_{0.75}\mathrm{Ni}_{0.25}(\mathrm{pc})\mathrm{I}$, $\mathrm{Cu}_{0.25}\mathrm{Ni}_{0.75}(\mathrm{pc})\mathrm{I}$, $\mathrm{Cu}_{0.9}\mathrm{H}_{2(0.1)}(\mathrm{pc})\mathrm{I}$, and $\mathrm{H}_2(\mathrm{pc})\mathrm{I}$.

The x-ray study was carried out using two methods. First, the so-called fixed-film fixed-crystal method originally used in the study of 1D conductors[15] allows performing a large survey of the reciprocal lattice. Second, the rotation/oscillation Weissenberg method allows the obtention of particular layers of the reciprocal lattice (zero- and upper-level layers) perpendicular to the rotation axis. As the *M*(pc)I organic compounds form needles elongated along the *c* direction, the crystals were

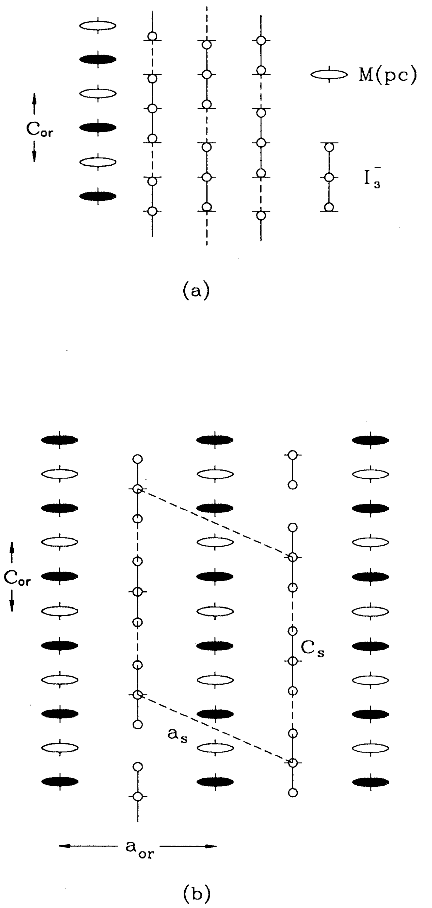

FIG. 1. (a) Disorder model for the iodine chains in *M*(pc)I according to Ref. 12. The three possible iodine chain arrangements are shown on the right. The *M*(pc) stack is shown on the left. White and black ellipses refer to the two *M*(pc) molecules staggered by 40°. (b) Projection of the ordered lattice along $b_S=b_{\mathrm{or}}$: $a_S=a_{\mathrm{or}}+c_{\mathrm{or}}$, $c_S=3c_{\mathrm{or}}$.

mounted on a goniometer head in order to permit rotation around this axis. Even if the crystal size was small, the crystal faces were clean and well defined so that nice x-ray patterns could be obtained with exposure times of one or two days. One crystal was installed on the cold finger of a cryocooler able to achieve temperatures between 290 and 20 K; the fixed-film fixed-crystal method was then employed. All the x-ray patterns were obtained by selecting the Cu $K\alpha$ radiation ($\lambda = 1.542$ Å) after (002) reflection on a doubly bent pyrolitic graphite monochromator. All five crystals were investigated at room temperature. Their x-ray diffraction patterns exhibit the same basic features. Here we will discuss mainly the results obtained on the $Cu_{0.25}Ni_{0.75}$(pc)I and $Cu_{0.75}Ni_{0.25}$(pc)I samples which, because of their larger size and good quality, were studied more completely. In addition, the second crystal was studied at 20 K by fixed-film fixed-crystal method. No major structural modification was observed upon cooling this crystal.

Figure 2(a) shows a fixed-film fixed-crystal x-ray pattern from $Cu_{0.75}Ni_{0.25}$(pc)I at room temperature taken with an orientation allowing a direct projection of the reciprocal planes perpendicular to the c direction on the film. In Fig. 2(a) these layers are labeled according to the organic (l_{or}) and iodine (l_{I}) reciprocal periodicities. In agreement with the original x-ray study of Schramm *et al.*[12] the third iodine layer was found to coincide with the second organic layer, which leads to the commensurate relationship between the organic and iodine periodicities along c: $2c_{\mathrm{I}} = 3c_{\mathrm{or}}$. However, in contrast to this study, all the iodine layers are now composed of sharp Bragg reflections, which means that a well-defined 3D order is established between the iodine chains. However, the interchain order is not perfect. A closer inspection of Fig. 2(a) reveals the existence of a weak diffuse scattering linking the Bragg reflections located on the $3n+1$ and $3n+2$ iodine layers (n integer), which means that a residual disorder still remains. The same observations have been done on the four other crystals investigated.

To characterize the 3D order we have recorded (hkl) reciprocal planes of the organic and iodine sublattices with the Weissenberg model. Figure 3(a) shows the zero-level ($hk0$) Weissenberg plane of $Cu_{0.25}Ni_{0.75}$(pc)I, which is common to the organic and iodine sublattices. We have also taken the organic reciprocal planes for $l_{\mathrm{or}} = 1$ and $l_{\mathrm{or}} = 2$. Again the $(hk2)_{\mathrm{or}}$ organic reciprocal plane was found to coincide with the $(hk3)_{\mathrm{I}}$ iodine reciprocal plane. From these data we confirm the systematic absence of $(0kl)_{\mathrm{or}}$ and $(hhl)_{\mathrm{or}}$ reflections with l_{or} odd and that the organic sublattice exhibits the tetragonal primitive Bravais lattice ($a_{\mathrm{or}} = b_{\mathrm{or}}, c_{\mathrm{or}}$) previously investigated by Schramm *et al.*,[12] with, according to the photographic measurements, $a_{\mathrm{or}} = 14.06(4)$ Å and $c_{\mathrm{or}} = 6.40(2)$ Å for $Cu_{0.25}Ni_{0.75}$(pc)I. We have also taken $(hkl)_{\mathrm{I}}$ reciprocal planes of the iodine sublattice with $l_{\mathrm{I}} = 1,2,4$. The Weissenberg layer $l_{\mathrm{I}} = 4$ is shown Fig. 3(b). Four lattices of spots can be identified in this layer. They are related by the fourfold tetragonal symmetry. Three of them are constituted of Bragg reflections having about the same intensity. The fourth lattice was made of Bragg reflections of much weaker intensity. This suggests the existence of four domains due to the four ways to couple the iodine chains between channels delimited by the tetragonal organic sublattice. The (a^*, c^*) reciprocal plane associated to one domain is shown in Fig. 4. It is in commensurate

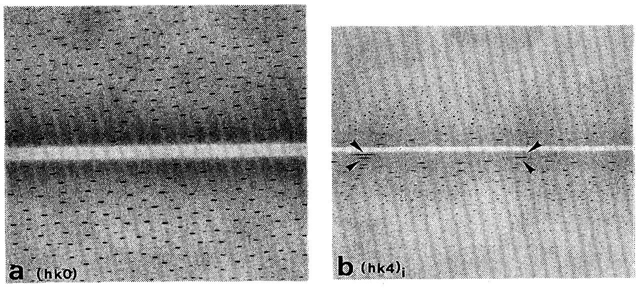

FIG. 3. X-ray diffraction Weissenberg photographs at 295 K of $Cu_{0.25}Ni_{0.75}$(pc)I: (a) zeroth-level Weissenberg photograph ($hk0$) common to the organic and iodine sublattices and (b) fourth-level Weissenberg photograph of iodine sublattice $(hk4)_{\mathrm{I}}$. In (b) the arrows point towards the equivalent Bragg reflections belonging to the reciprocal space of the four domains discussed in the text.

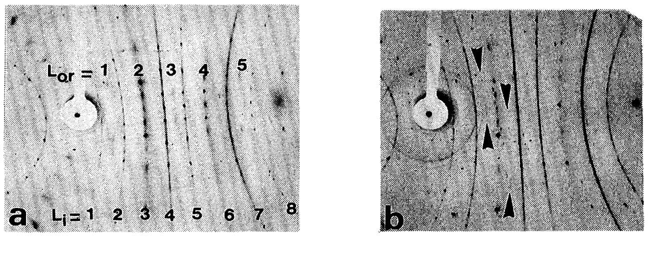

FIG. 2. Fixed-film fixed-crystal x-ray diffraction pattern for the crystal $Cu_{0.75}Ni_{0.25}$(pc)I at (a) 295 K and (b) 20 K. In (a) the layers of Bragg reflections perpendicular to the c direction are labeled according to the organic (l_{or}) and iodine (l_{I}) sublattice reciprocal periods. In (b) the arrows point towards Bragg reflections due to the intermodulation of the M(pc) and I_3^- sublattices.

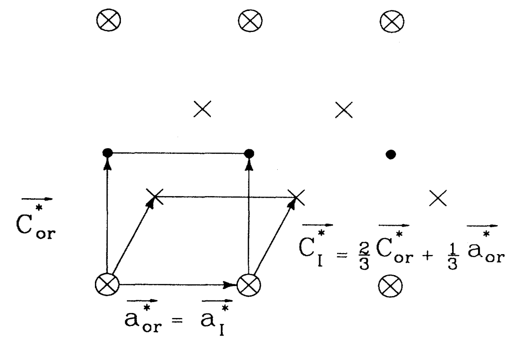

FIG. 4. (a^*, c^*) reciprocal plane of an iodine domain and its relationship with the organic reciprocal lattice.

relationship with the organic reciprocal space; for this domain

$$a_{\rm I}^* = a_{\rm or}^*, \quad b_{\rm I}^* = b_{\rm or}^*, \quad c_{\rm I}^* = \tfrac{2}{3}c_{\rm or}^* + \tfrac{1}{3}a_{\rm or}^* .$$

In the other three domains $a_{\rm I}^*$ and $b_{\rm I}^*$ remain the same but $c_{\rm I}^*$ takes the three other orientations generated by the tetragonal symmetry, namely, $c_{\rm I}^* = \frac{2}{3}c_{\rm or}^* - \frac{1}{3}a_{\rm or}^*$ and $c_{\rm I}^* = \frac{2}{3}c_{\rm or}^* \pm \frac{1}{3}b_{\rm or}^*$. The unit cell parameters of the iodine sublattice associated to the reciprocal space shown in Fig. 4 are related to the organic tetragonal frame by the relationship

$$a_{\rm I} = a_{\rm or} + c_{\rm or}, \quad b_{\rm I} = b_{\rm or}, \quad c_{\rm I} = \tfrac{3}{2}c_{\rm or} .$$

This iodine sublattice frame is monoclinic with the binary axis along $b_{\rm I}$. There is one $\rm I_3^-$ per unit cell whose volume is $\frac{2}{3}$ that of the organic cell. A structure factor analysis of the intensity of the iodine Bragg reflections shows that the $\rm I_3^-$ units (of I-I intramolecular distance of 2.97 Å) are along the $c_{\rm I}$ direction. The iodine sublattice space group is thus $P2/m$. It is also possible to incorporate both sublattices in a monoclinic supercell containing two $\rm I_3^-$ and six M(pc) units. Its projection along b_S is shown Fig. 1(b). The supercell parameters are

$$a_S = a_{\rm or} + c_{\rm or}, \quad b_S = b_{\rm or}, \quad c_S = 3c_{\rm or} .$$

The space group of maximal symmetry, built with the symmetry elements common to $P4/mcc$ and $P2/m$, is $P2/c$. This supercell should lead to additional $(hkl)_s$ layers of Bragg reflections for $l_s = 1, 5, 7, 10$ (i.e., for l_S not a multiple of 2 or 3). Such layers, due to the intermodulation of the two sublattice periodicities, have been detected by the fixed-film fixed-crystal method in all the samples investigated. Bragg reflections belonging to the layers $l_S = 5$ and 7 are shown [arrows in Fig. 2(b)] in the x-ray pattern taken from $\rm Cu_{0.75}N_{0.25}$(pc)I at 20 K. They are of very weak intensity, which means that the interaction between the $\rm I_3^-$ and M(pc) sublattices is weak. Moreover, a structure factor analysis of such reflections of intermodulation would be necessary in order to determine the exact position of the $\rm I_3^-$ units with respect to the M(pc) molecules.

The iodine ordering, shown in Fig. 1(b), where two $\rm I_3^-$ units belonging to neighboring channels distant of $a_{\rm or}$ are successively shifted by $c_{\rm or}$, certainly represents a configuration which minimizes the Coulomb repulsion between the $\rm I_3^-$. This ordering can be achieved by four equivalent different manners within the tetragonal organic sublattice: shifts of $\pm c_{\rm or}$ along $a_{\rm or}$ or of $\pm c_{\rm or}$ along $b_{\rm or}$. If the shift between the first neighbor chains randomly takes one of these four possibilities, the interchannel disorder observed in the first synthesized crystals[12] will be realized. The long-range interchannel order of Fig. 1(b) requires an *identical* shift between all the first-neighbor pairs of iodine chains. It must be stabilized by Coulomb interactions going beyond the first neighbors. The $l_{\rm I} = 3n+1$ and $l_{\rm I} = 3n+2$ diffuse lines observed in the x-ray patterns of Fig. 2 could correspond to faults in the sequence of identical shifts and to domain boundaries. We have analyzed this residual disorder by measuring with a microdensitometer, as a function of $l_{\rm I}$, the diffuse intensity $\rm I_{\it D}$ exhibited by the x-ray pattern of Fig. 2(b). $\mathrm{I}_D(l_{\rm I})$ can be accounted for by the model of disorder developed in Ref. 12 where there is a long-range order of $\rm I_3^-$ units along the $c_{\rm I}$ direction, but random displacement of neighboring chains as shown in Fig. 1(a). Using expression (2) of Ref. 12 together with an additional Debye-Waller factor, accounting for the interchain disorder, one gets

$$I_D = |f_{\rm I}|^2 \left[1 + 2\cos\left[2\pi l_{\rm I} \frac{u}{c_{\rm I}} \right] \right]^2 \times \left[1 - \left[\frac{1 + 2\cos(2\pi l_{\rm I}/3)}{3} \right]^2 \right] \times \exp\left[- \left[\frac{2\pi l_{\rm I}}{c_{\rm I}} \right]^2 \langle \delta^2 \rangle \right] , \qquad (1)$$

where $f_{\rm I}$ is the iodine atomic form factor, u is the I-I intramolecular distance, and in the Debye-Waller factor $\langle \delta^2 \rangle$ is the mean-square displacement of the $\rm I_3^-$ unit along $c_{\rm I}$. The experimental data, shown in Fig. 5, can be well fitted by this expression. The fit leads to an I-I distance of 2.98(2) Å, a value which agrees quite well with the one (3 Å) found in Ref. 12 and the one (2.97 Å) deduced from the structure factor analysis of the iodine Bragg reflections. The Debye-Waller factor at 20 K leads to a fluctuation of the positions of the $\rm I_3^-$ units $\sqrt{\langle \delta^2 \rangle} = 0.18(1)$ Å which is comparable to the distance d required to displace the I atoms from an average lattice site to form $\rm I_3^-$ units ($d = c_{\rm I}/3 - u = 0.22$ Å). This value means that, in addition to the interchain disorder, a sizable intrachain static disorder also remains.

Finally, it is interesting to remark that the same type of $\rm I_3^-$ ordering is found in the TMA-TCNQ-I organic conductors[16] and that the synthesis of this salt has also re-

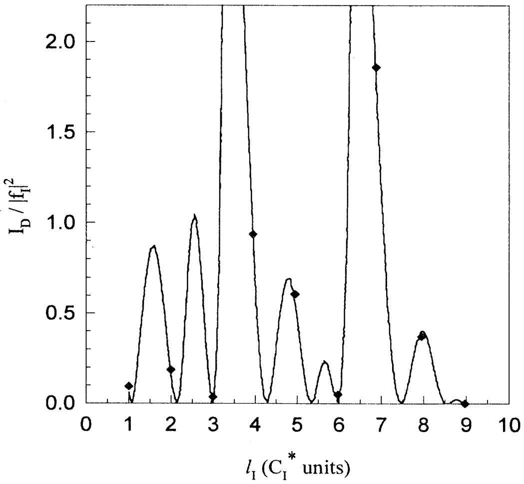

FIG. 5. Dependence of the reduced iodine diffuse intensity $\mathrm{I}_D/|f_I|^2$ as a function of the iodine Miller index $l_{\rm I}$. The data are shown by a dot at each integer $I_{\rm I}$ value and the continuous line is the fit given by expression (1).

vealed[17] an important interchannel iodine disorder. Such an interchannel disorder was enough to suppress the Peierls-like transition of TMA-TCNQ-I.[18]

We have shown that in recently synthesized crystals there is a lateral order between the iodine chains. Thus the observed improvement of the electronic properties of *M*(pc)I may be associated with the iodine ordering, as well as with the improved purity of the *M*(pc). Our structural investigation shows that there is a weak but finite coupling between the iodine and *M*(pc) sublattices. Thus any interchannel disorder within the iodine sublattice should induce some disorder in the *M*(pc) stacks in between four iodine channels. This disorder could be the principal reason of limitation of the electrical conductivity in the first samples synthesized. But it can be hardly invoked as the main cause of the absence of a clear metal-insulator transition at ambient pressure in the newly synthesized Ni(pc)I samples.

Now we will consider the 1D dispersion of the conduction band structure of the *M*(pc) stacks taking into account the symmetry of the new supercell. As the iodine forms I_3^- units, there is a charge transfer of $\frac{1}{3}$ of an electron per *M*(pc) molecule. This yields to a $\frac{5}{6}$ filled conduction band[19,4] with a Fermi wave vector given by $k_F=\frac{5}{6}(\pi/c_m)$, where c_m is the *M*(pc)-*M*(pc) spacing of the stack. Such a situation is illustrated in the 1D tight-binding band structure represented in Fig. 6. As two adjacent *M*(pc) units are staggered by 40°, the organic repeat periodicity is $c_{\mathrm{or}}=2c_m$. Thus the band structure must be folded at $\pm k_{\mathrm{or}}=\pm\pi/c_{\mathrm{or}}\equiv\pm\pi/2c_m$. However, as the two *M*(pc) molecules of the unit cell are related by the *c* glide plane symmetry, the band degeneracy at $\pm k_{\mathrm{or}}$ is not removed. We will now consider the effect of the I_3^- periodic potential on the 1D band structure. The iodine period c_I will thus open gaps (shown by circles on the band structure shown in Fig. 6) at the wave vectors $\pm\pi/c_I$ $(=\pm\frac{2}{3}\pi/c_{\mathrm{or}}=\pm\frac{1}{3}\pi/c_m)$ and its harmonics. For a supercell of period c_S, the band structure will be further folded at $\pm k_S=\pm\pi/c_S$ $(=\pm\pi/3c_{\mathrm{or}}=\pm\pi/6c_m)$. Figure 6 shows that the $2k_F$ wave vector now corresponds to the reciprocal periodicity $2k_S$. However, if the supercell space group is $P2/c$ the band folding degeneracy at $\pm k_S$ will not be removed because of the presence of the *c* glide plane symmetry. With such a high symmetry the metallic character is maintained, in agreement with the experimental finding. But any structural distortion breaking the *c* glide plane symmetry will open a gap at $\pm k_F$ in the band structure, which will lead to a Peierls metal-insulator phase transition. In such a case the two I_3^- units and the six *M*(pc) units of the supercell will no longer be related by symmetry. Such a structural transition could be achieved for moderate pressures in Ni(pc)I as a result of a $2k_F$ CDW or a $2k_F$ SDW instability. However, at larger pressures additional effects, such as the warping of the Fermi surface due to interstack interactions, could suppress the full Peierls gap opening and restore metallic (or semimetallic) properties.

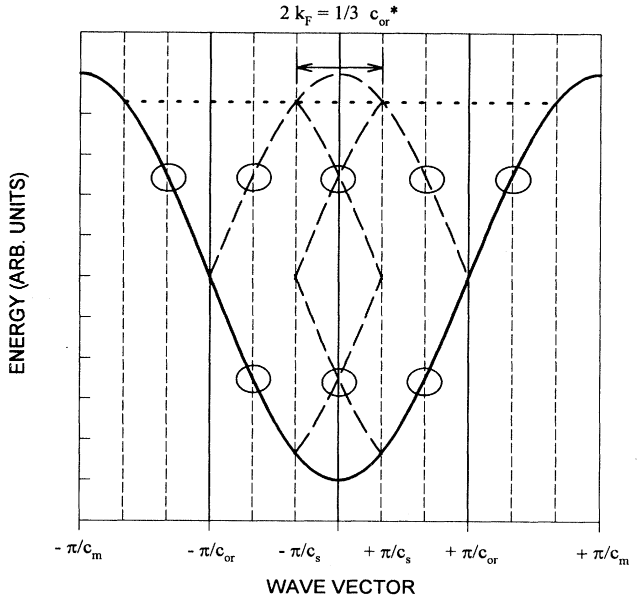

FIG. 6. 1D tight-binding dispersion of the conduction band structure of *M*(pc)I in stacking direction and its folding due to the various periodicities considered in the text. Open circles denote wave vectors at which the interaction between the I_3^- and *M*(pc) sublattices will open a gap.

In conclusion and in contrast to what was generally accepted for the structure of $M(\mathrm{pc})^{+0.33}(I_3^-)_{1/3}$, our x-ray study has shown that in the newly synthesized materials the iodine anions are not only ordered along the chain direction but that the chains themselves are ordered relatively to each other at all temperatures. This has been confirmed on various *M*(pc)I crystals, where $M=H_2$, Cu/Ni, and Cu/H_2. The tetragonal structure with the space group $P4/mcc$ has to be modified to a monoclinic structure with the space group $P2/c$. The new unit cell includes six *M*(pc) molecules and two tri-iodine anions and has a lattice periodicity along the *c* axis which is three times the organic one. The electronic structure taken into account by this $P2/c$ symmetry is consistent with the 1D metallic transport properties observed for these crystals. Under pressure this symmetry could be lowered with the result of opening a gap at the Fermi level. This picture could explain the experimental observations reported for Ni(pc)I. All the physical properties will have to be rediscussed in relationship with these structural findings.

This work was supported by the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (FCAR) du Québec, by the Natural Sciences and Engineering Research Council (NSERC) of Canada, and by the National Science Foundation of the U.S.A. [Grant No. DMR-9144513 (B.M.H.); Northwestern University Materials Research Center, Grant No. DMR-9120521].

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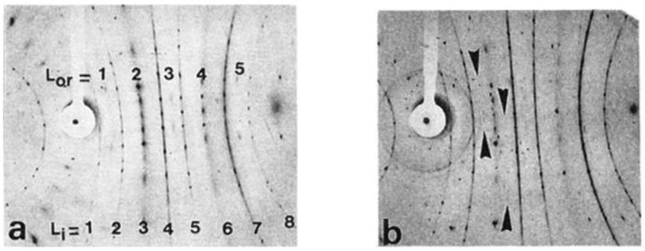

FIG. 2. Fixed-film fixed-crystal x-ray diffraction pattern for the crystal $\mathrm{Cu}_{0.75}\mathrm{Ni}_{0.25}$(pc)I at (a) 295 K and (b) 20 K. In (a) the layers of Bragg reflections perpendicular to the c direction are labeled according to the organic (l_{or}) and iodine (l_{I}) sublattice reciprocal periods. In (b) the arrows point towards Bragg reflections due to the intermodulation of the M(pc) and I_3^- sublattices.

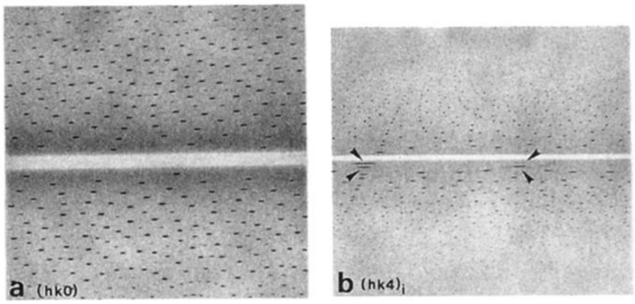

FIG. 3. X-ray diffraction Weissenberg photographs at 295 K of $Cu_{0.25}Ni_{0.75}$(pc)I: (a) zeroth-level Weissenberg photograph ($hk0$) common to the organic and iodine sublattices and (b) fourth-level Weissenberg photograph of iodine sublattice $(hk4)_I$. In (b) the arrows point towards the equivalent Bragg reflections belonging to the reciprocal space of the four domains discussed in the text.