January 1991

Interaction of Pyridine with Ba2CaSr2Cu20x

Juana Acrivos
San Jose State University, juana.acrivos@sjsu.edu

C. Lin
Cambridge University

Recommended Citation

Juana Acrivos and C. Lin. "Interaction of Pyridine with Ba2CaSr2Cu20x" *Journal de Physique IV* (1991): 325-330. https://doi.org/10.1051/jp4:1991537

92.

INTERACTION OF PYRIDINE WITH $Bi_2CaSr_2Cu_2O_x$

J. V. Acrivos[+,*] *and C. T. Lin*[*]

San Jose' State University, San Jose' CA 95192-0101,[*]
and IRC in Superconductivity, Cambridge University,[+]

Abstract: The adsorption of of pyridine on single crystals of $Bi_2CaSr_2Cu_2O_x$ has been followed by optical microscopy on the crystal surface where a blue solution is formed as a first step of reaction. The superconducting properties of the single crystal and its structure were monitored by ac susceptibility and x-ray diffraction measurements. The results (as observed by the growth of the blue solution boundary versus time with $D_{aa} = 3.7x10^{-10}$ cm^2/s.) indicate that the reaction starts at nucleation sites on the basal surface of the crystal. The edges of the crystal also show blue nucleation sites but these do not grow with time. The changes in the ac susceptibility indicate that the superconducting volume has increased. This can be explained by the intercalation of pyridine, although the x-ray data are not very conclusive.

I. Introduction.

The layer structure shown by all of the new cuprate superconductors suggests that the covalent layers (e.g., CuO_2, BiO_2,..) are intercalated in between ionic layers layers (i.e., the layers containing the oxygen ions and the other cations which constitute the single crystal).(1) Also many of these materials can be pealed with adhesive tape indicating that the forces holding some of the layers are as weak as in other layer compounds such as graphite. This suggests that the superconducting cuprates can undergo intercalation reactions in a similar way as graphite and the layer dichalcogenides.(2) The properties of $Bi_2CaSr_2Cu_2O_x$ exposed to pyridine have been investigated in search for for evidence of the effects of intercalation on superconductivity.

II. Experimental.

The single crystals were prepared as described elsewhere,(3) and the reaction of the crystals with Merck, reagent grade pyridine was carried out in a closed desiccator containig $CaCl_2$ drying agent. At the IRC for superconductivity, the changes in the crystal surface were observed using an OLYMPUS BH2-M Universal Series microscope, equipped with a 35 mm. camera; the ac susceptibility measurements from 4 to 100 K were carried out using a Lakeshore Model 7000 ac susceptometer that was calibrated with Pb standard spheres and the 00ℓ diffractions were measured with a DIFFRACTINEL System. The crystals do not appear to be attacked by moisture before or after the reaction with pyridine.

III. Results.

The surface of a single crystal of $Bi_2CaSr_2Cu_2O_x$ exposed to pyridine is shown in Figure 1.

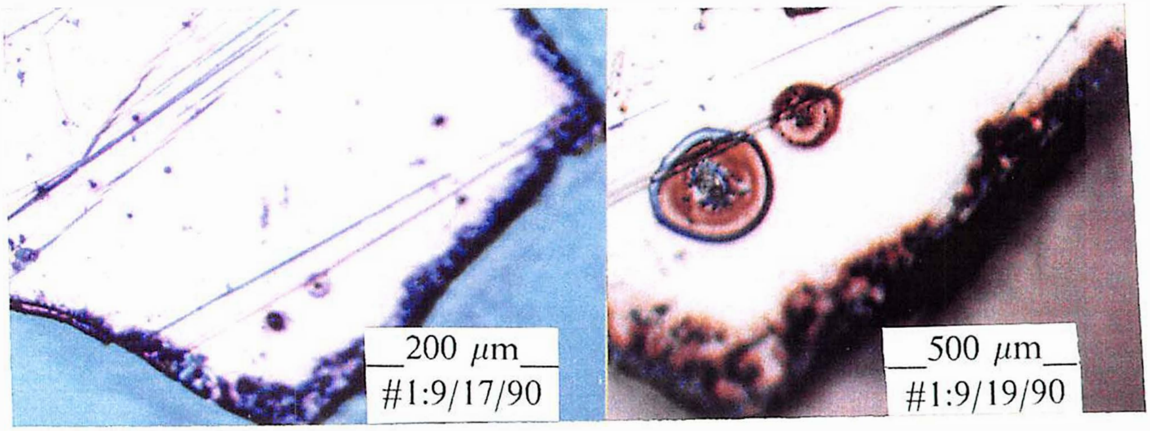


Fig. 1: Photograph of the surface optical reflection of crystal #1 $Bi_2CaSr_2Cu_2O_x$, exposed to pyridine vapor and liquid for 8 and 10 days, respectively, inside the desiccator. The light source is the halogen vapor lamp of the microscope. The blue center is characteristic of all the nucleation sites.

Figure 2 shows other nucleation centers observed.

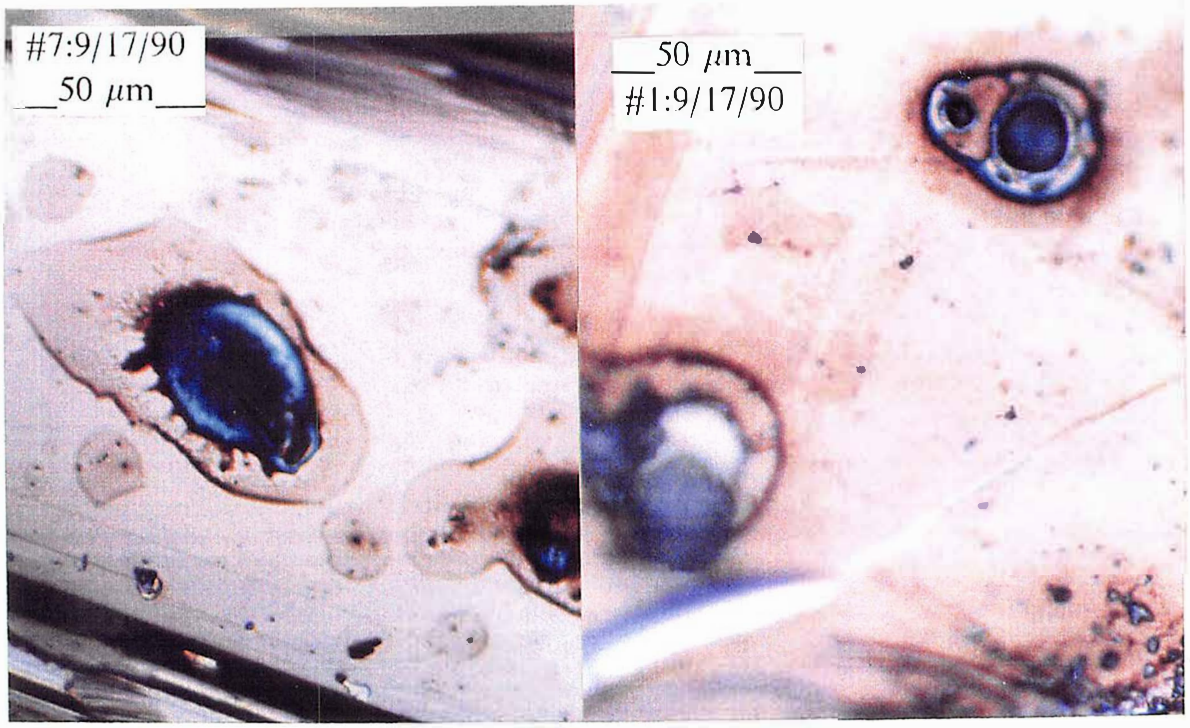


Fig. 2: Photograph of the surface optical reflection of crystals #7 and #1 $Bi_2CaSr_2Cu_2O_x$, exposed to pyridine vapor and liquid for eight days inside the desiccator. The light source is the halogen vapor lamp of the microscope. The blue center is characteristic for all the nucleation sites.

Here both the basal plane and the crystal edges show the presence of blue nucleation sites. However only the nucleation centers formed on the basal plane grow with time. The largest nucleation center shown is an active reaction site. It grows with a blue edge front of 50μm radius and a width of several μm. Other reaction sites on the basal plane that show brown edged radii do not grow with time. The lines on the crystal surface are not affected by the exposure to pyridine. They appear to be crystal growth steps. Thus the fact that the circular fronts for the two nucleation centers shown in Figure 1 go under the growth steps suggests that the diffusion proceeds under the basal plane, i.e., this offers evidence that intercalation of the first few layers has occurred. The growth of the active reaction site in Figure 1 may be used to estimate the basal diffusion coefficient of the intercalant. In two days, the radius of the site shown grows from 40 to 120 μm. This indicates that the combined time for reaction and diffusion gives an effective diffusion coefficient in two dimensions of $D_{aa} = 3.7 \times 10^{-10}$ cm^2/s. However the growth of the reaction sites appears to be limited by the size and the presence of other sites nearby. The reaction sites formed near the single crystal edges are very close together and do not grow with time. This is the first direct observation that, only the reaction sites formed on the basal plane of the crystal lead to subsequent intercalation. Indirect information based on the decrease of the reflecting power of the 00ℓ and hk0 x-ray diffractions for single crystals of of TaS_2 in the symmetric position, exposed to NH_3 gas, led to the mechanism hypothesis that the intercalation of layer compounds starts by the formation of reactions sites on the basal surface of the crystal.(2) These observations on the cuprate superconductors not only support the hypothesis, they confirm it with additional information, namely that under the attack of an intercalant as, gas, reaction sites are indeed formed at the crystal edges, as common sense would suggest. The new important datum, however, is that the sites must be isolated, as on the basal surface of the crystal in order for the intercalation reaction to proceed into the bulk crystal. The chemical reaction may be written as:

$$\phi_0 + n\ I(g) = \phi_I \tag{1}$$

where ϕ_0 and ϕ_I represent the original and intercalated phases respectively and I(g) is the pyridine intercalant. Evidence for intercalation can be obtained only qualitatively by x-ray diffraction. For a single crystal in the symmetric position, diffraction data only give information on the the respective c-axes. Here $c_0 = 30.63$ A,(1) and if a stage 1 intercalated compound is produced, $c_I = c_0 + d_I$ where d_I represents the thickness of the intercalant layer. For a stage 1 complex Xiang et al.,[4] have found that, in iodine intercalated $Bi_2CaSr_2Cu_2O_8$, the 008 and 0010 diffractions of the pristine phase ϕ_0 coincide with the 0010 and 0012 diffractions of the intercalated phase ϕ_I, whilst other diffractions confirm the presence of the intercalated phase. Here a similar case occurs and a d_I of 7.5 A can explain the new strong Cu $K_\alpha$diffraction observed at $2\theta = 37.7^0$ for ϕ_I. Changes in the relative intensity of the diffraction lines have also been observed here but, the changes in the ac susceptibility are more conclusive in the matter of intercalation.

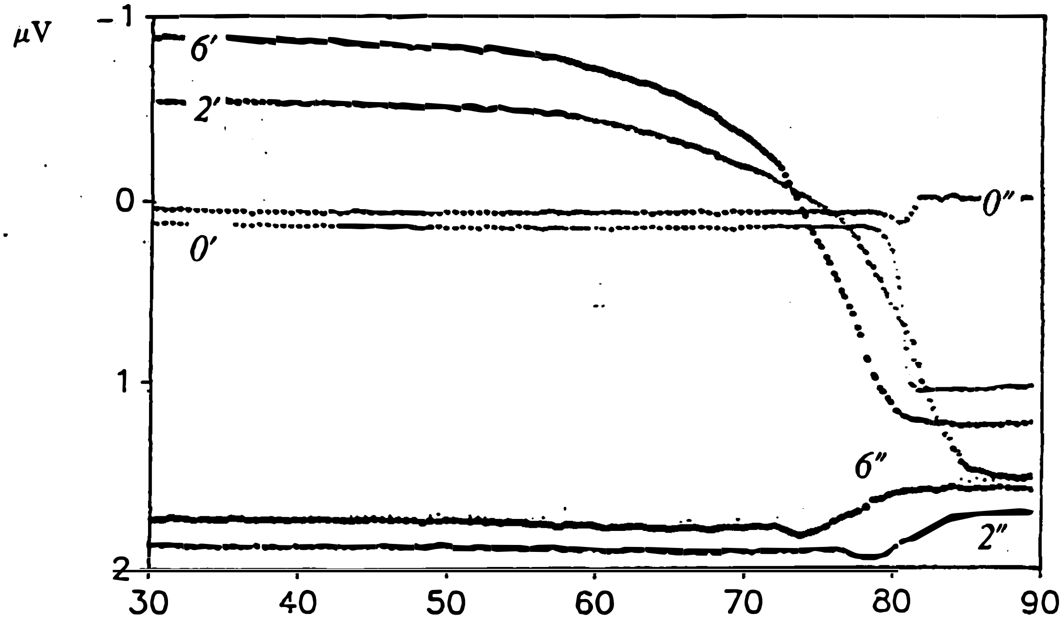
The results of the ac susceptibility measurements are shown in Figure 3. The effective complex susceptibility, $X_e' - iX_e''$ was measured in the field $H = H_0 \cos(2\pi ft)$, at the frequency $f = 333.33$ Hz and amplitudes $H_0 = 30$ and 15 μT in order to verify that saturation field effects are not present. No differences were observed when the data was normalized at 30 μT. The data in Figure 3 are normalized at 30 μT. The demagnetization correction is very important for the flat single crystals used.(5,6) The ac susceptibility measurements shown in Figure 3 record the output voltage v of the lock-in-detector of the Lakeshore 7000 susceptometer. The effective susceptibility is then given by:(6)

$$X_e = \alpha v/(VH_0 f) \tag{2}$$

where α is the calibration constant and V is the sample volume. The true susceptibility is obtained by introducing the demagnetization correction which obtains:(5)

$$X = X_e/(1 - DX_e) \tag{3}$$

Here D is the demagnetization factor which may be calculated given the sample shape. D = 1/3 for spheres and for superconducting Pb spheres X = -1, obtains X_e = -1.5 which allows us to use the calibration for the instrument ($1\mu V = 2.0 \times 10^{-5} cm^3$ when H_0 = 0.3 mT and f = 333.333 Hz to within a 3% accuracy),(7) i.e., $\alpha = 3\mu Tm^3/Vs$ in relation (2) obtains $X_{e,0}'$ = -5.8 to within 25% accuracy in Figure 3 where the highest error is introduced in determining the sample volume as follows.



T(K) AT 1K/min RATE OF INCREASE

Fig. 3: Effective susceptibility for crystal #9 ($Bi_2CaSr_2Cu_2O_x$, before and after exposure to pyridine in the desiccator for a number of days d). The ordinate units are μV but the zero point at T above T_c is displaced for each curve, i.e., the voltage output is given by the difference between the value near 30 K and say 90 K. $X_{e,d}$ identifies the susceptibility measured after d days of exposure and each curve is designated by the number of days of reaction with pyridine d' or d'' for the in phase or out of phase susceptibility respectively.

The sample is a flat crystal and all the measurements are made with c// H_0. The $2*10^{-4}$ g crystal with a basal area given by the side dimensions, a*b = $2*0.5\ mm^2$, has a volume, estimated from the weight using the crystalline density ($6.53\ g/cm^3$) V = $30 \times 10^{-12}\ m^3$ and an overall thickness, d = V/ab = 30 μm. Then the calibration curves, (5) obtain for b/a = 0.25 and d/a = 0.015, $D(\phi_0)$ = 0.9528 for the pristine phase ϕ_0. The strongest evidence for intercalation now is obtained by the change in $X_{e,d}$. The data in Figure 3 show that after intercalation the signal has increased, i.e., the in phase effective susceptibility ratio is:

$$r_X = X_{e,d}'/X_{e,0}' = 2.45 \tag{4}$$

independent of d = 2, 6 and 9 days of reaction. This suggests that a change in demagnetization factor has caused the increase in $X_{e,d}$. For a completely intercalated sample, the volume V_I increases, i.e.,

$$r_V = V_I/V_0 = c_I/c_0 = 1.24 \tag{5}$$

and the calibration curves,(5) obtain $D(\phi_I) = 0.9376$ for the intercalated phase. However at some intermediate time where the above measurements were made the ratio:

$$r = r_X/r_V \tag{6}$$

determines the amplitude of the effective susceptibility, i.e., from relations (3) to (6) it follows that the ratio of the true susceptibility for the intercalated and pristine sample is:

$$X(\phi_I)\ /X(\phi_0) = r(1\text{-}D(\phi_0)X_e(\phi_0))/(1\text{-}rD(\phi_I)X_e(\phi_0)) \tag{7}$$

The calibration gives for the data in Figure 3, $X_{e,0}' = -5.8$ and, assuming that intercalation is complete, $X_{e,d}' = -11.5$. Then in relation (7):

$$r_t = X(\phi_I)/X(\phi_0) = 1.1 \tag{8}$$

i.e., the susceptibility is unchanged to within 10% at 30 K for the data in Figure 3. The deviation from unity may be due to the fact that the sample is not completely intercalated and it may also be due to the error introduced by the uncertainty in the sample volume. The physical significance here is, that for superconductors, the changes in the amplitudes of the effective susceptibility, X_e are a very sensitive measure of the change in the sample volume through the demagnetization factor where,

$$r_t/r = 1 + (r_t D(\phi_I) - D(\phi_0))X_e(\phi_0) \tag{9}$$

The effect of the pyridine intercalant on the superconducting transition temperature of $Bi_2CaSr_2Cu_2O_x$ is to lower it by a few degrees (5 K in Figure 3).

IV. Discussion.

The two dimensional nature of the cuprate superconductors is confirmed by the intercalation reaction. The large unit cell for $Bi_2CaSr_2Cu_2O_x$ (with c_0 = 30.63 A) could explain the intercalation by pyridine (this work), and by iodine.(4) There are other cases where the intercalation of chlorine and fluorine has increased the superconducting transition temperature of $Y_1Ba_2Cu_3O_{6.7}$ as follows. Perrin et al.,(8,9) have intercalated $Y_1Ba_2Cu_3O_x$, x = 6, 6.7 and 7. by reaction (1) with intercalant gases CCl_4, F_2 and Cl_2. The saturation values depend on x, i.e., the final compounds are $Y_1Ba_2Cu_3O_6Cl_{2.38}$, $Y_1Ba_2Cu_3O_{6.7}Cl_{1.18}$ and $Y_1Ba_2Cu_3O_7Cl_{0.65}$, which suggests that the reaction is controlled by charge transfer and that $Y_1Ba_2Cu_3O_7$ is still an electron donor. The compound $Y_1Ba_2Cu_3O_{6.7}Cl_y$ shows a transition temperature to superconductivity above 85 K for y greater than 0.1.

The reaction with electron donors has also been reported, e.g., $Y_1Ba_2Cu_3O_7$ reacting with butyl lithium produces the complex $Y_1Ba_2Cu_3O_7Li_x$,(10) which is superconducting near 92 K for x less than 0.5, suggesting that both acceptor and donor adducts can intercalate the superconducting layer cuprates. Pyridine can be both a donor and an acceptor.

V. Conclusions.

The observation of a blue solution formed at the reaction sites of pyridine intercalant on the basal surface of a layered superconducting cuprate indicates that one of the first steps in the intercalation of metals and semimetals is chemisorption and that, most probably, charge transfer is involved in this step. The insertion of the adduct in between the two dimensional networks provided by the metal appears to be restricted by the space available for diffusion of the products from the initial reaction site. A high concentration of reaction sites (as formed near the crystal edges) does not lead to diffusion into the solid.

The superconducting properties of the pyridine intercalated $Bi_2CaSr_2Cu_2O_x$ are changed as would be expected in a charge transfer reaction. Here the superconducting transition temperature T_c is decreased by 5 K. In other cases, the intercalation of strong electron acceptors such as Cl_2, increase T_c in $Y_1Ba_2Cu_3O_{6.7}$. It appears that the Fermi level of the host solid plays an important role in determining whether T_c increases or decreases by the effect of charge transfer. This effect has also been observed for the layer dichalcogenides.(2)

VI. Acknowledgements.

This work was done under the auspices of a sabbatical leave from SJSU during the academic year 1990/1991, a Visiting Commoner, Lucy Cavendish Fellowship (fall 1990) and NSF Grants DMR 8921163 and INT 8922483. It was inspired by the renewed association with the PCS Group of the Cavendish Laboratory, that under tutelage of Dr. A.D. Yoffe, Reader, developed the original field of "Intercalation Physics and Chemistry in Low Dimensional Solids" from 1960 to 1990 and thereby paved the way for the development of the new field of layer superconducting cuprates. JVA wishes to thank Drs. A. D. Yoffe and W. Y. Liang for the hospitality received during the sabbatical leave from SJSU at the Cavendish Laboratory and the IRC for Superconductivity during the fall semester 1990 and Dr. E. Clementi for the invitation to the Center for Scientific and Engineering Computations of the International Business Machines Corporation during the spring and summer of 1991. Last but not least thanks are due to the Abbe′ Gerard Lepoutre for making all the Colloque Weyls possible. This work on charge transfer in solids is dedicated to Gerard Lepoutre.

VII. References.

1. Ginsberg, DM, *Physical Properties of High Temperature Superconductors II,* World Scientific, Singapore, (1990)
2. Acrivos, JV, *Physics and Chemistry of Electrons and Ions in Condensed Matter, Acrivos, J.V., Mott, N.F. and Yoffe, A.D., ed., NATO ASI Series,* D. Reidel (1984) p. 491.
3. Lin, CT, *IRC for Superconductivity, to be published.*
4. Xiang, XD, McKernan, S, Vareka, WA, Zetl, A, Corkill, JL, Barbee III, TW, and Cohen, ML, *Nature 348 (1990) 145.*
5. Goldfarb, RB, and Minervini, JV, *Rev. Sci. Instrum. 55 (1984) 761.*
6. Lakeshore Cryogenics Model 7000, *Manual (1989) 1.*
7. Cooper, JR, *IRC for Superconductivity, private communication, (1990).*
8. Perrin, C, Pena, O, Sergent, M, Fonteneau, G, and Lucas, J, *Europhysics Letters 11 (1990) 181 and references therein.*
9. Perrin, C, Pena, O, and Sergent, M, *Proceedings Garmish-Partenkirchen Meeting, May (1990).*
10. Varez, A, Moran, E, and Alario-Franco, MA, *Solid State Communications 76 (1990) 917.*

$$\phi_0 + n\ I(g) = \phi_I \qquad (1)$$

where ϕ_0 and ϕ_I represent the original and intercalated phases respectively and I(g) is the pyridine intercalant.

The effective complex susceptibility,

$X_e' - iX_e''$

was measured in the field $H = H_0 \cos(2\pi ft)$,
at $f = 333.33$ Hz and amplitudes $H_0 = 30$ and 15 μT

$$X_e = \alpha v/(VH_0f) \qquad (2)$$

$$X = X_e/(1 - DX_e) \qquad (3)$$

$$r_X = X_{e,d}'/X_{e,0}' = 2.45 \qquad (4)$$

$$r_V = V_I/V_0 = c_I/c_0 = 1.24 \qquad (5)$$

$$r = r_X/r_V = 1.98 \qquad (6)$$

$$X(\phi_I)/X(\phi_0) = r(1-D(\phi_0)X_e(\phi_0))/(1-rD(\phi_I)X_e(\phi_0)) \qquad (7)$$

$$r_t = X(\phi_I)/X(\phi_0) = 1.1 \qquad (8)$$

$$r_t/r = 1 + (r_tD(\phi_I) - D(\phi_0))X_e(\phi_0) \qquad (9)$$

1. The two dimensional nature of the cuprate superconductors leads to the intercalation reaction.

2. The large unit cell for $Bi_2CaSr_2Cu_2O_x$ could explain the intercalation by pyridine and by iodine.

3. There are other cases where the intercalation of $Cl_2$and F_2 has increased the superconducting transition temperature of $Y_1Ba_2Cu_3O_{6.7}$ The saturation values depend on x, i.e., the final compounds are $Y_1Ba_2Cu_3O_6Cl_{2.38}$,$Y_1Ba_2Cu_3O_{6.7}Cl_{1.18}$,$Y_1Ba_2Cu_3O_7Cl_{0.65}$, $Y_1Ba_2Cu_3O_7$ is still an electron donor.

4. $Y_1Ba_2Cu_3O_{6.7}Cl_y$ shows a transition temperature to superconductivity above 85 K for y greater than 0.1.

5. The reaction with electron donors has also been reported, e.g., $Y_1Ba_2Cu_3O_7$ reacting with butyl lithium produces the complex $Y_1Ba_2Cu_3O_7Li_x$ superconducting near 92 K for x less than 0.5.

6. Pyridine can be both a donor and an acceptor.

7. The observation of a blue solution formed at the reaction sites of pyridine intercalant on the basal surface of a layered cuprate indicates that one of the first steps in the intercalation of metals and semi-metals is chemisorption and that, most probably, charge transfer is involved in this step.

8. The insertion of the adduct in between the two dimensional net-works provided by the metal appears to be restricted by the space available for diffusion of the products from the initial reaction site. A high concentration of reaction sites (as formed near the crystal edges) does not lead to diffusion into the solid.

9. The superconducting properties of the pyridine intercalated $Bi_2CaSr_2Cu_2O_x$ are changed as would be expected in a charge transfer reaction.