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STRUCTURAL STUDIES OF INTERCALANTS

DISCLAIMER

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Abstract

The structure of stage 2 potassium intercalated graphite, KC_{24}, is discussed in both the ordered and disordered phases. A one-dimensional model is used to illustrate the qualitative features of the KC_{24} diffraction patterns.

1. Introduction

The existence of graphite intercalation compounds has been known for almost fifty years. These systems have been of recent interst because of the high basal-plane conductivity and the highly two-dimensional nature of the electronic structure in some of these compounds [1]. Early x-ray structural studies on the stage 2 alkali metal compounds [2] MC_{24} (M = K,Rb, Cs) have shown the existence of an order-disorder transition. Following these studies a-axis resistivity measurements [3] showed not one, but two anomalies. The structural nature of these two anomalies has since been revealed by x-ray studies [4] for stage 2 potassium. Figure 1 shows a schematic phase diagram for KC_{24}, where above approximately 125K the potassium lattice is "disordered", between 125K and about 95K there is an ordered compound and at 95K there is a structural transition which involves the stacking of the potassium layers.

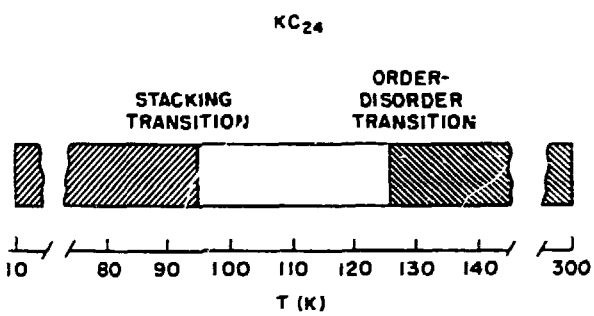

Fig.1 Phase diagram of KC_{24} as a function of temperature

The temperature evolution of the ordered phase at T = 125K was studied with x-ray scattering [4,5] and the order-disorder transition appeared continuous. Of particular interest was the observation of c-axis stacking faults in this intermediate phase [4] with ABC stacking (FCC like). BAK and DOMANY [7] studied the order-disorder transition in the presence of these stacking faults and found it to be a smeared first order transition which is consistent with the data [4,5].

The lower transition was shown to be structural in nature where the stacking went from ABCABC... to ABAB... [4,6] (an FCC to HCP like stacking). Thus, below this transition the c-axis stacking of the potassium no longer follows the graphite matrix and there is no evidence for stacking faults in the low temperature phase. Recent c-axis resitivity measurements [8], which should be sensitive only to the loss of a scattering mechanism at the lower transition, indeed show only one anomaly at the lower temperature.

The only remaining questions then are the in plane structure of the intermediate and low temperature phases. In the following sections these questions will be addressed albeit in a qualitative fashion and without any definitive conclusions. Clearly detailed crystallographic studies are needed to give the structural parameters of these interesting compounds.

2. X-ray scattering results and discussion

2.1 Experimental details

All the experimental data is on stage 2 potassium graphite. The sample is highly oriented pyrolytic graphite (HOPG) and intercalated by the standard two bulb method. The sample dimensions are typically 10 x 5 x 0.1 mm^3 and the c-axis is always in the scattering plane. After inercalation the sample was transferred to a beryllium can from its glass container in an inert atmosphere. The beryllium can reduces the background significantly. The can is attached to the cold finger of a closed cycle refrigerator that allows the temperature to be varied continuously from room temperature to about 10K with a stability of typ 0.05K.

The triple axis x-ray spectrometer uses a 1kW sealed Cu x-ray tube as a source. The beam is monochromated with a pyrolytic graphite monochromator, (00 2) reflection, set to reflect the CuK_α radiation giving an incident wavevector of $4.075A^{-1}$. An 00 2 graphite analyzing crystal is used on the third axis and in combination with the (002) monochromator gives a wavevector resolution, ΔQ, of typically $.02A^{-1}$ at Q's of the order of $2A^{-1}$.

2.2 Disordered phase results

Scattering measurements have been made, referring to Fig. 1, in both the high temperature, disorderd phase, above 125K discussed below and the intermediate phase 95K < T < 125K discussed in the following section. As stated earlier the sample was intercalated from an HOPG sample and oriented with the c-axis in the scattering plane. Therefore scans perpendicular to the c-axis, $Q = (h,0)$, are powder scans with $h = |h\bar{i} + k\bar{j}|$ and thus the orientational dependence of the in plane scattered intensity of the potassium with respect to the graphite is lost.

A typical data set at T = 130K is shown in Fig. 2. Plotted is the intensity as a function of h for $Q = (h,0)$. As noted previously [5] there is no variation of intensity with ℓ for fixed $h = h_0$, that is for $Q = (h_0,\ell)$. What is seen immediately is a fairly sharp feature at $Q = (1.2,0)$ and a broad feature at $Q = (2.40,0)$ typical of "liquid" like scattering. The sharp feature around $Q = (2.93,0)$ is the tail of the graphite (101) peak [4]. Between the features at $Q = (1.2,0)$ and $(2.4,0)$ is another sharp feature at $Q = (1.7,0)$. These results are in contrast to the study of CsC_{24} [9] which shows a "liquid" like scattering and is well understood in terms of a close-packed 2 dimensional Cs liquid.

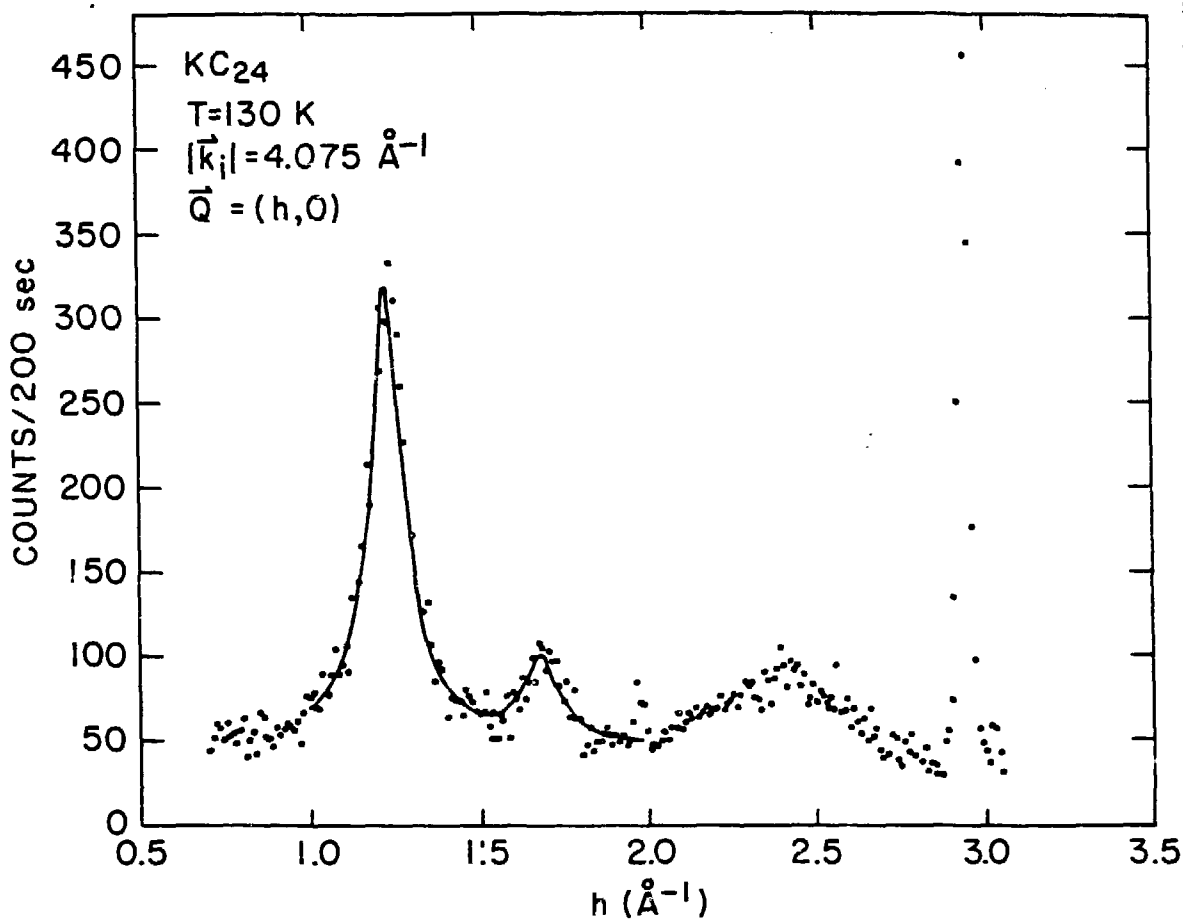

Fig.2 Scan along Q = (h,0) at 130K in the disordered phase. The solid line is a fit of two Lorentzians.

In order to understand the differences between CsC_{24} and KC_{24} the two sharp features at Q = (1.2,0) and Q = (1.7,0) have been fit with two Lorentzians.

$$I(Q) = \frac{I_{01}}{1+\Gamma^2(Q-Q_1)^2} + \frac{I_{02}}{1+\Gamma^2(Q-Q_2)^2} + I_{Bkgd} \cdot \qquad (1)$$

The peak postions, intensities, and a single width were free parameters. The solid line in Fig. 2 is a fit and a summary of parameters as a function of temperature is given in Fig. 3. As the order-disorder transition is approached from above the in plane correlations grow as can be seen in the increase of Γ. The potassium-potassium distance decreases with decreasing temperature as well, noted by the variation of $|\bar{Q}_1|$. However, the decrease of $|\bar{Q}_1|$ is always matched by an increase of $|\bar{Q}_2|$ such that the sum $|\bar{Q}_1|+|\bar{Q}_2|$ is independent of temperature and equal to to the graphite (100) wavevector.

Thus unlike the Cs system where the disordered alkali metal is constrained to lie between the graphite layers but is otherwise independent of the matrix the K system is already "affected" by the in plane graphite structure far above its ordering temperature.

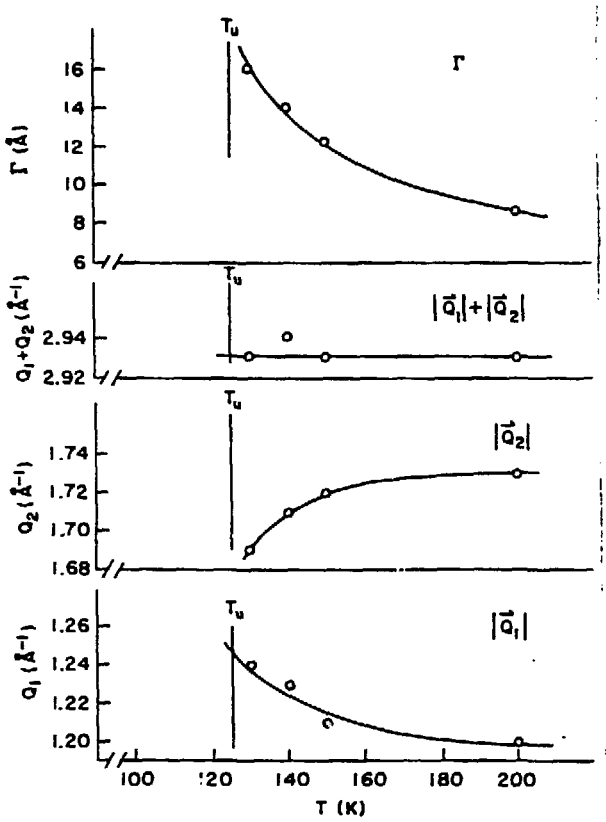

Fig.3 Parameters of the fits to scans along Q = (h,0) in the disordered phase. Γ is the width of the two Lorentzians, $\vec{Q}_1$ and $\vec{Q}_2$ the peak positions and $\vec{Q}_1+\vec{Q}_2$ the sum of the positions. The solid lines are guides to the eye.

2.3 Intemediate phase results

As the temperature is lowered through the order-disorder transition into the intermediate phase the peaks sharpen and develop three dimensional character in the direction perpendicular to the layers [4,5]. An earlier study [4] has discussed the presence of stacking faults in both the graphite matrix and the intercalant lattice in this phase. A typical scan along the ℓ = 0 layer, Q = (h,0) at 105K is shown in Fig. 4. In contrast to the broad features above 125K the peaks are resolution limited in the plane. The solid lines in the figure are merely guides to the eye. The relatively sharp feature at h = 1.7 remains and in fact has grown relatively in intensity. The positions of the features of this scattering pattern seem to be well understood and will be addressed in the following discussion.

2.4 Discussion

The understanding of diffraction data involves both position and intensity. First is to understand the positions of the maxima. The peak positions shown in Fig. 4 as well as other experiments on KC_{24} [4-6] can be understood geometrically as coming from two lattices, the graphite matrix and the intercalant as well as sums and differences of the wavevectors of these two lattices. This is eveidence for a modulated structure and following OVERHAUSER [10] directly both the positions and relative intensities can be calculated. The interaction betwe n the intercalant and the graphite will cause displacements of the atomic positions

$$\vec{U}(\vec{L}) = \vec{A} \sin (\vec{q}.\vec{L} + \phi)$$

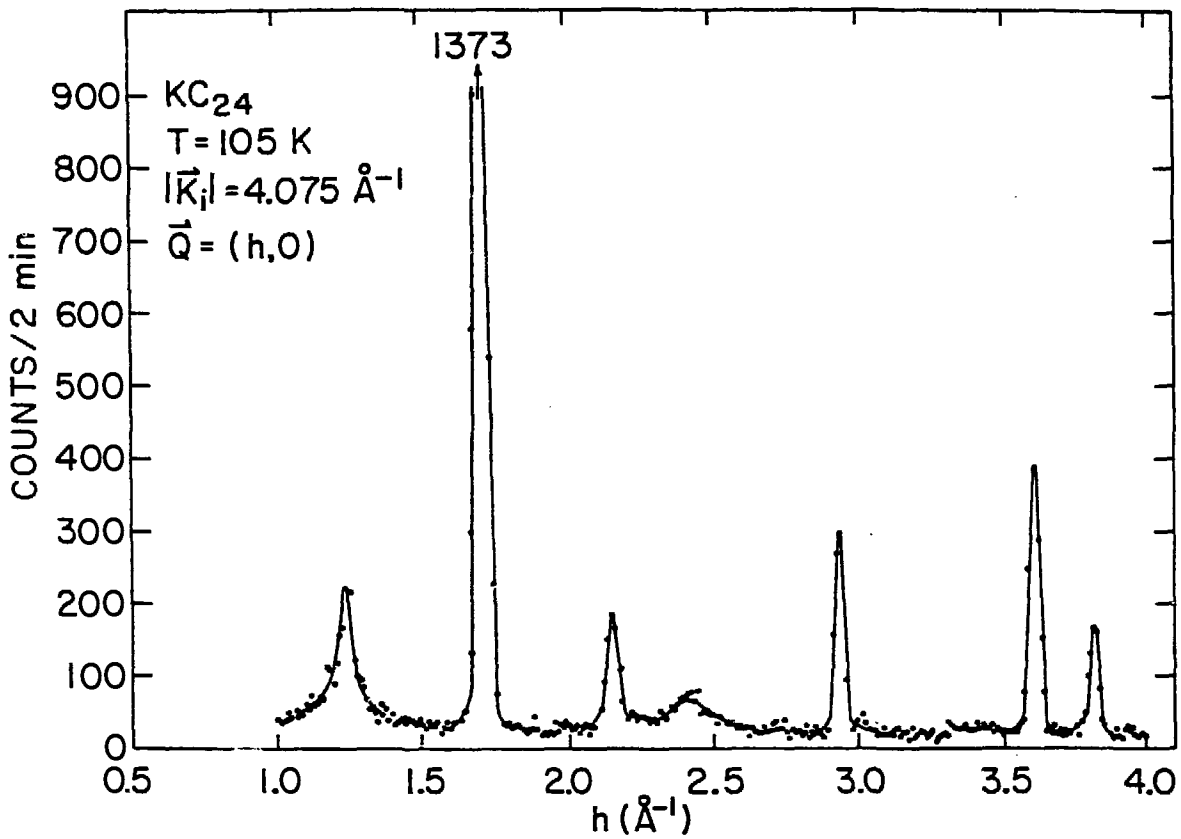

Fig.4 Scan along Q = (h,0) at 105K in the intermediate phase. The solid lines are guides to the eye.

where $\bar{U}$ is the displacement, $\bar{L}$ is the vector to the ℓth atom, $\bar{q}$ is a wave vector describing the modulation, $\bar{A}$ is the modulation amplitude and ϕ a phase factor. Assuming that one of the two lattices is undistorted then the density of the distorted lattice can be written as

$$\rho'(\bar{r}) = \sum_{\bar{L}} \rho(\bar{L})\, \delta\, (\bar{r} - \bar{L} - \bar{A} \sin (\bar{q} \cdot \bar{L}))$$

neglecting the phase. The elastic scattering amplitude is just the Fourier transform of the scattering density

$$F(\bar{Q}) = \int \rho'(\bar{r})\, e^{i\bar{Q} \cdot \bar{r}}\, d\bar{r}$$

which is, substituting from above

$$F(\bar{Q}) = \sum_{\bar{L}} f_{\bar{L}}(\bar{Q})\, e^{iQ \cdot (\bar{L} + \bar{A} \sin \bar{q} \cdot \bar{L})}$$

where $f_{\bar{L}}(\bar{Q})$ is the atomic scattering factor for the ℓth atom. Assuming that $f_{\bar{L}}(\bar{Q}) = f(\bar{Q})$ independent of $\bar{L}$ and using the Jacobi-Anger generating function for Bessel functions gives

$$F(\bar{Q}) = f(\bar{Q}) \sum_{L,n} J_n (\bar{Q}\cdot\bar{A})\, e^{i(\bar{Q} + n\bar{q}) \cdot \bar{L}} .$$

$F(\bar{Q})$ is only non-zero when $\bar{Q} \pm n\bar{q} = \bar{G}$ so the diffraction maxima of the modulated lattice occur when $\bar{Q} = \bar{G} \pm n\bar{q}$ where $\bar{G}$ is a reciprocal lattice vector of the "modulated" lattice, and $\bar{q}$ is the wavevector of the modulation. For $n = 0$ the peaks are the Bragg peaks of the modulated lattice, for $\bar{G} = 0$ there are peaks of the undistorted lattice and $n \neq 0$, $\bar{G} \neq 0$ are the sums and differences of the two lattices.

The relative intensities of the main Bragg peaks of the modulated lattice ($n = 0$) and the first order satellites ($n = \pm 1$) can be calculated. Neglecting thermal motion and phase fluctuations

$$I \propto F^2(\bar{Q}).$$

For $n = 0$, $\bar{Q} = \bar{G}$ and $F \propto J_0(\bar{Q}.\bar{A})$ and for $n = \pm 1$, $\bar{Q} = \bar{G} \pm \bar{q}$ and $F \propto J_1(\bar{Q}.\bar{A})$. Generally, the amplitude of the modulation is small so that the Bessel functions are in the limit of small arguments, X, where

$$J_n (x) \sim X^{2n} .$$

However, the magnitude of the modulation peak, the feature at $Q = (1.7,0)$ in Fig. 4, indicates that the modulation is not small. Referring to Fig. 5 where $J_0^2(X)$ and $J_1^2(X)$ are plotted versus their arguments, one can see that in fact around $x = 2.2$ there is a zero in $J_0^2(X)$ so that some primary Bragg peaks could have very small intensities.

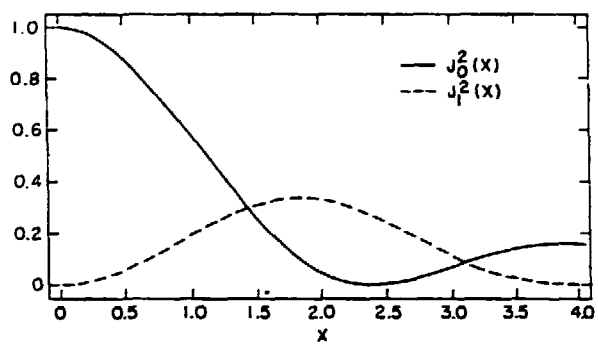

Fig.5 The square of the zeroth and first order Bessel functions versus their arguments

Using this formulation for the intensities, one can look qualitatively at the intermediate phase intensities in some simple limits, assuming the modulation is purely longitudinal, either rigid graphite with modulated potassium or the reverse. Roughly, then, for rigid graphite the ratio of the potassium (110) to the first order satellite, I_{SAT}, at $Q = (1.71,0)$ gives $|\bar{A}_L| = 1.35 \pm 0.2$ A for $\bar{U}(\bar{L}) = \bar{A}_L \sin(\bar{q} \cdot \bar{L} + \phi)$ with $\bar{q}$ equal to the graphite (100) wavevector. Using this value of $|\bar{A}_L|$ predicts a ratio of I(100) to I_{SAT}. of 2:3 and measured is roughly 1:2 but the existence of the faulted structure makes it difficult to estimate the integrated intensity of the (100) potassium peak.

With the assumption of rigid potassium and modulated graphite and q the potassium (100) wavevector the ratio of the graphite (110) intensity to the

satellite gives $|\overline{A_L}| = 0.18 \pm .05$. Using this value however and comparing the graphite (104) to the satellite predicts a ratio of 9.6 compared with the measured value of 3.6. Furthermore, with a rigid potassium lattice the fall off in intensity of the potassium peaks I(100)/I(110) - 4.5 cannot be explained. However, with the modulation of the potassium lattice and referring to Fig. 5, with $|\overline{A_L}| = 1.35$, the (110) potassium peak falls near a zero in $J_0^2(X)$ while the (100) peak does not.

Finally, with this argument in hand it is interesting to ask, could the potassium ions sit "over" the centers of graphite hexagons, be registered, and still give a diffraction pattern that appears incommensurate with the graphite matrix. There are several observations that support this argument. First, in the early work of PARRY and co-workers [1], in order to explain the intensity ratios of the graphite peaks in the disordered phase a contribution of 1/6 of a potassium atom over each carbon hexagon (2 carbon atoms per hexagon and 12 potassium atoms per layer) was required. Second, the extended x-ray absorption fine structure measurements of CASWELL et. al. [11] are consistent with the potassium ions centered over the carbon hexagons. Lastly, the value of $|\overline{A_L}|$ for the modulated potassium calculated roughly above is just the difference between the average near neighbor distance in stage 2 and stage 1. The stage 1 compound KC_8 is a commensurate 2 x 2 structure and thus the stage 2 compound may be made up of "islands" of stage 1, perhaps as small as two or three atoms.

These ideas can be addressed for a simple one-dimensional model to see the qualitative features of the diffraction pattern from registered, disordered lattices. The model [12] consists of an infinite chain with atoms placed at two spacings na and (n + 1)a, where 'a' is the near neighbor spacing along the chain. The atoms are then 'placed' on the chain by the flip of one of two coins. After choosing the first spacing, do by the flip of a coin, if $d_0 = (n + 1)a$ then one uses a 'coin' with the probability of d_1 being (n+1)a equal to p' and na being $q' = 1 - p'$. For $d_0 = na$ a second 'coin' is used with probability, p, for $d_1 = (n + 1)a$ and $q = 1 - p$ for $d_1 = na$. With these rules then, by varying p and p' one can go from a completely random lattice, $p = p' = .5$ to complete order, spacing n, n + 1, n, n + 1..., with $p' = 0$, $p = 1$. GRIMM, AXE, and KROHNKE [12] derived an analytic form for the structure factor, S(Q), and for $n = 2$, and several values of p and p' S(Q) is plotted as a function of Q in Fig. 6. X is just the average spacing, (n + (n + 1))/2. If the system were completely ordered there would be sharp, Bragg peaks at Q = 0.2, 0.4, 0.6, 0.8 and so on, however even in the random system, there remain two sharp features one at Q roughly (1/X) and one at (1 - 1/X). These peaks could be interpreted easily as an "incommensurate" peak and a modulation satellite and are reminiscent of the features seen in the disordered phase of KC_{24}, Fig. 2. As the system orders $p \to 1$, $p' \to 0$ these features become sharp but still slightly in-commensurate, as can be seen in the progression from (a) to (d) in Fig. 6. This, too, is similiar to the behavior of KC_{24} in the intermediate phase.

The features of a two dimensional system using the observed 'average' lattice for the potassium and then forcing the potassium atoms to sit over the centers of the nearest graphite hexagons has been calculated [13] by computer and yields the ovserved peak positions for KC_{24} in the intermediate phase. This can be considered as an extreme of a modulation.

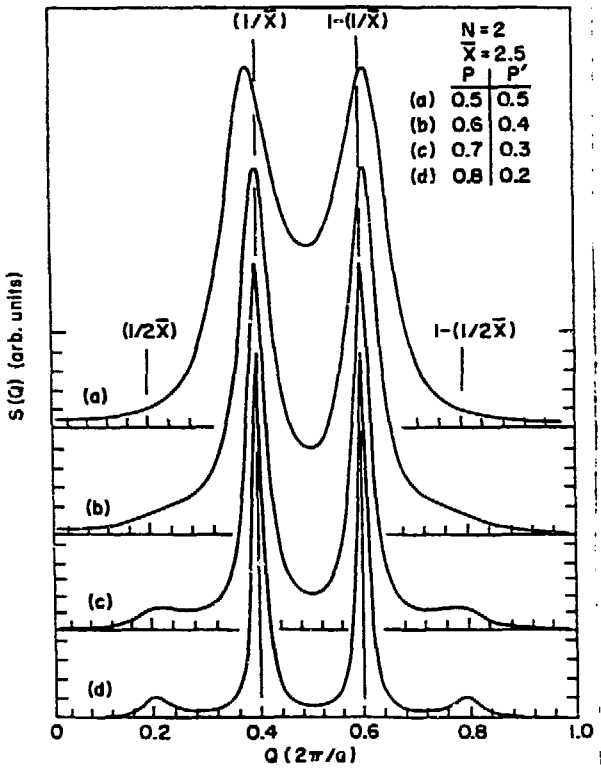

Fig.6 S(Q) versus Q for one-dimensional chains going from random occupation, panel (a) to almost ordered, panel (d). The average separeation between atoms on the chain is 2.5a

3. Summary

The phase diagram of KC_{24} is now reasonably understood but only a qualitative picture is available for the in-plane structure. This system may be an example of a registered disordered system or it could be simply incommensurate. Some of these issues could be addressed by calculation and others by detailed line shape measurement in the intermediate phase or a complete structure analysis of a single crystal. In any case there are still things to be done.

Acknowledgments

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References

1 G.M.T. Foley, C. Zeller, E.R. Falardeau and F. L. Vogel, Solid State Commun. 24, 371 (1977); F. Batallan, J. Bok, I. Rosenman and J. Melin, Phys. Rev. Lett. 41, 330 (1978).

2 G.S. Parry, D.E. Nixon, D.M. Lester and B.C. Levene, J. Phys. C2, 2156 (1969); G.S. Parry and D.E. Nixon, Nature (London) 216, 909 (1967).

3 David G. Onn, G.M.T. Foley and J.E. Fischer, Mater. Sci. Eng. 31, 271 (1977).

4 J.B. Hastings, W.D. Ellenson and J.E. Fischer, Phys. Rev. Lett. 42, 1552 (1979).

5 H. Zabel, S.C. Moss, N. Caswell and S.A. Solin, Phys. Rev. Lett. 43, 2022 (1979).

6 H. Zabel, Ordering in Two Dimensions, edited by S.K. Sinha (North-Holland, Amsterdam, 1981).

7 Per Bak and Eytan Domany, Phys. Rev. B23, 1320 (1981).

8 Phan and Fuerst, unpublished.

9 R. Clarke, N. Caswell, S.A. Solin and P.M. Horn, Phys. Rev. Lett. 43, 2018 (1979).

10 A. Overhauser, Phys. Rev. B3, 3173 (1971).

11 N. Caswell, S.A. Solin, T.M. Hayer and S.J. Hunter, Physica 99B, 463 (1980).

12 H. Grimm, J.D. Axe and G. Krohnke, BNL 29083 (1981).

13 S.B. DiCenzo, unpublished.