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Short-range stacking order in the layered material diaquabis(salicylato)copper(II), studied by x-ray and Raman scattering

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Abstract. The present work is concerned with new ways of understanding and describing short-range stacking order in layered materials. The x-ray pattern from several layered materials, in the present work exemplified by $\text{Cu}(\text{C}_6\text{H}_4(\text{OH})\text{COO})_2 \cdot (\text{H}_2\text{O})_2$ (DSC), consists of alternating discrete Bragg spots and diffuse, modulated lines, indicating a large degree of disorder, which is interpreted as being associated with the stacking of the rigid layers. From a detailed study of the shape and widths of the diffuse component, a pseudo-spin model is developed, from which short-range order parameters are derived, amounting to first- and second-nearest neighbour coupling of an Ising model. This approach is contrary to models describing the crystal as consisting of a mixture of ordered and disordered phases. The ordering parameters are sample dependent, but for a given sample they are temperature independent, as concluded from Raman studies between 50 K and room temperature.

1. Introduction

Crystalline materials always show some *time-dependent* deviation from the ideally ordered, periodic state, due to molecular and lattice vibrations. For many materials also static, *time-dependent* deviation from order may be present. Such materials contain molecular groups where several, energetically almost equivalent configurations are possible. Layered materials often belong to this category, due to various equivalent choices of layer stacking sequences. It is the nature of such stacking disorder which will be the theme of the present work.

The presence of disorder may be revealed in diffraction patterns by the appearance of diffuse scattering (in addition to the sharp Bragg peaks). In several layered materials (Jagner 1985, Durovic 1979), among them the title material (Dornberger-Schiff and Malinovski 1966, Jagner *et al* 1976) such diffuse streaks have been observed. However, superimposed on the diffuse streaks were also observed rather sharp intensity maxima at integer (or half-integer) values of the layer normal index l . These sharp features were interpreted as being due to Bragg scattering, from which structural information could be extracted but one had to assume that each crystal consists of a mixture of a disordered phase and two ordered phases, denoted maximum degree of order phases one (MDO_1) and two (MDO_2) (Dornberger-Schiff 1966).

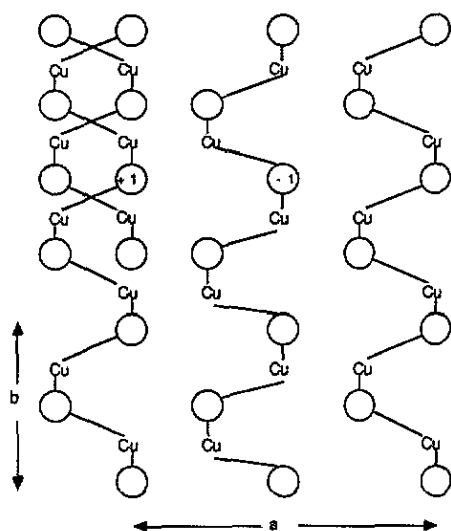


Figure 1. Schematic representation of the DSC-structure viewed along c . The chains run along b , with salicylic groups (circles) linked by Cu. A given layer (open symbols) together with the layer beneath (shaded symbols) forms a double layer. The next double-layer origin of the +1-marked ring may be either below this ring (MDO₁ case) or below the -1-marked ring (MDO₂ case).

The present work was undertaken to reexamine the notion of mixed phase crystals. The title compound was chosen because single crystals of good quality of this compound are relatively easy to grow.

New x-ray data were taken both with film and detector scans. As will be described in the paper, detailed peak shape and peak width analyses were undertaken leading to the conclusion that only short-range stacking order is present.

2. The crystal structure

The crystal structure DSC was solved by Jagner *et al* (1976). The layers consist of infinite zig-zag chains of salicylic groups and Cu (see figure 1), adjacent chains being linked together by H-bonds to form the rigid layers. Neighbouring layers are connected by van der Waals interactions, which are responsible for the crystal cleavage. In fact neighbouring layers are mirror images of each other.

In their structural work Jagner *et al* (1976) found evidence for the presence of two forms, denoted MDO forms: an orthorhombic one (MDO₁) with space group $Pca2_1$, and cell dimensions $c = 31.547 \text{ \AA}$ (normal to the layers), $b = 11.795 \text{ \AA}$ (parallel to the chains) and $a = 7.73 \text{ \AA}$; and a monoclinic one (MDO₂) with space group $P2_1/a$, with the corresponding dimensions close to those of the MDO₁ form.

The difference between the two forms is the stacking of doubled layers: whereas for MDO₁ there is one double layer per orthorhombic unit cell, the double layers being stacked on top of each other along the c -axis, for the MDO₂ form, neighbouring double layers are shifted by half the a -axis (figure 2). Therefore, in the orthorhombic reference frame the c -axis of MDO₂ is doubled, corresponding to new Bragg peaks at half- l -index values.

The structure may be described in a compact way by introducing the discrete variable $S_n = \pm 1$: $(+1)^n$ for MDO₁, $(-1)^n$ for MDO₂.

The shift vector t_n for double-layer n may be written as

$$t_n = nc + (1 - S_n)a/4. \quad (1)$$

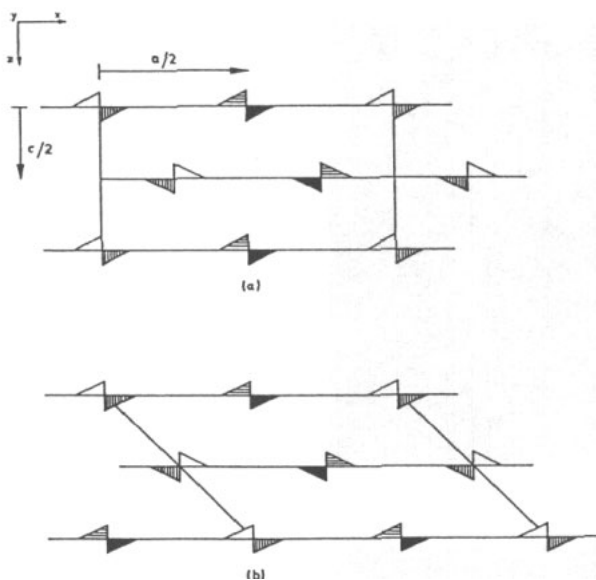


Figure 2. Schematic representation of stacking of layers in (a) the MDO_1 structure and (b) the MDO_2 structure. Empty triangles at level y ; full triangles at level $-y$; vertical shading at level $\frac{1}{2} + y$; horizontal shading at level $\frac{1}{2} - y$.

We see that the MDO_1 form is a 'ferromagnetically' ordered form of the pseudo-spin S_n , whereas MDO_2 is an 'antiferromagnetic' one. As we shall see in the following section, our samples are not of the ordered forms, but possess a layer disorder with a considerable degree of short-range order.

3. Experiment

Crystals were prepared at room temperature by adding 0.2 M $CuSO_4$ solution to the double volume of 0.2 M salicylic acid and 0.2 M NaOH. The solution was allowed to evaporate slowly over a few days, giving green needle-shaped crystals of DSC.

Five crystals were selected for the present x-ray diffraction study, their size being of the order of $3 \times 1 \times 0.2$ mm. The crystal edges coincide with orthorhombic a , b and c , respectively.

The studies were performed with Cu-radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature on a two-axis diffractometer equipped with both film and point detector options (Samuelson *et al* 1987).

Figure 3(a) shows an oscillation exposure around the a -axis, with the characteristic pattern of diffuse lines for $h = \text{odd}$, but normal Bragg spots for $h = \text{even}$. Figure 3(b) shows a Weissenberg-type exposure of the diffuse scattering at the $h = 1$ level.

The diffuse lines along the c^* -axis are modulated by the variation of the double-layer structure factor. Furthermore, and to some extent sample dependent, it is observed that the diffuse lines have superimposed on them an intensity variation periodic in l , with maxima where l is integral (sometimes even at half integers too). In the solution of the structure (Jagner *et al* 1976 these peaks were treated as Bragg peaks. However, we find that their widths are considerably broader than the instrumental width, as may be seen

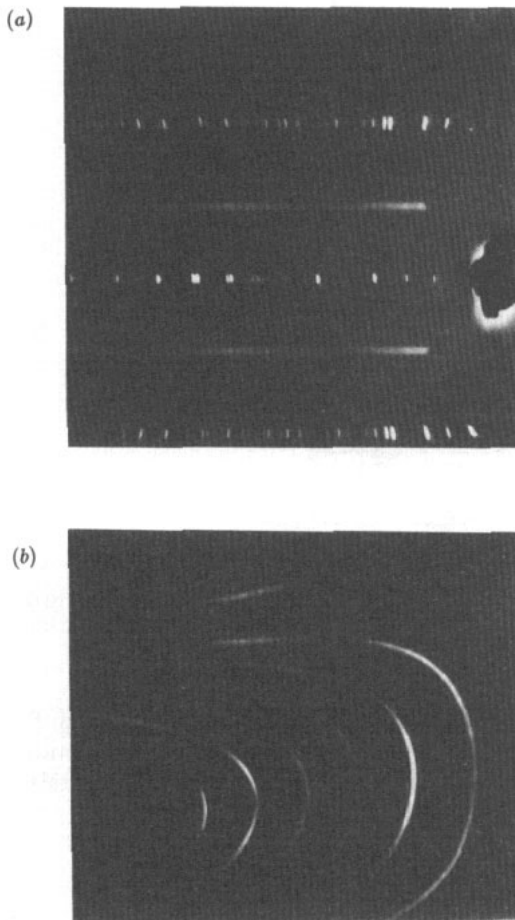


Figure 3. (a) Oscillation exposure around the a -axis, film distance 95 mm, $\lambda = 1.5418 \text{ \AA}$. Layers from below: $h = -2, -1, 0, 1, 2$. (b) Weissenberg exposure at the $h = 1$ layer, taken with the two-axes climbing detector instrument LOFTE (Samuelsen *et al* 1987). The vertical direction corresponds to the crystal turn angle and the horizontal direction from right to left corresponds to the scattering angle. The diffuse streaks ($1kl$) run along l , with k increasing (from 1) from right to left (lower part of figure). The streaks along l are seen to be continuous with some modulation, and with spots superimposed upon them (for integer l -values).

in figure 4, where the true Bragg peak 245 is compared with the diffuse peak 154. The two peaks have nearly identical scattering angles, yet the diffuse peak is broader by a factor 2.5. In addition, resolution estimation for the instrument leads to the same conclusion.

4. Model and correlation function

The presence of diffuse lines along e^* strongly indicates a stacking disorder of the layers (the stacking direction is c). Furthermore, the diffuse lines occur for $h = \text{odd}$, being compatible with a shift disorder of magnitude $\frac{1}{2}a$. One may thus account quantitatively for the observation by imposing a disorder of the double layer shift (1). For the pseudo-spin variable S_n we introduce

$$S_n = (\pm 1)^n S_a + s_n \quad (2)$$

where S_a is the average value (the order parameter), s_n is a fluctuation term defined such

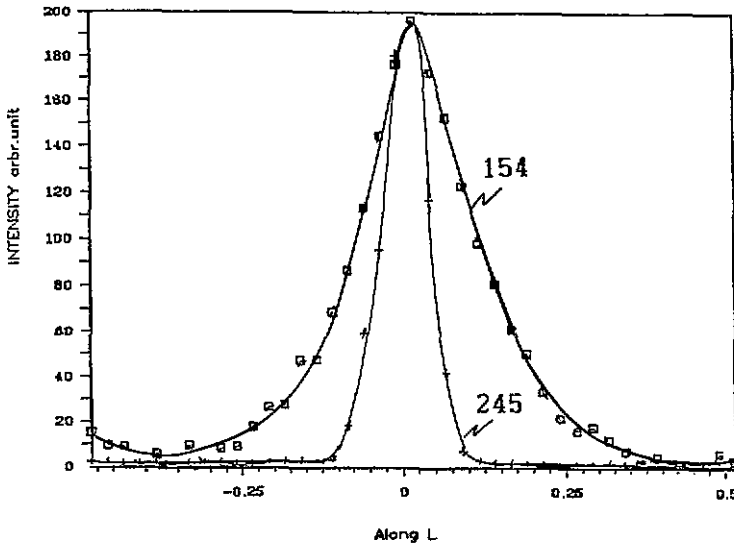


Figure 4. Comparison of the observed width along l of the Bragg peak 245 and the diffuse peak at (154), background corrected. The scattering angles are very similar (41.08° and 41.64° , respectively).

that $\langle s_n \rangle = 0$, and ± 1 applies for the MOD₁ and MDO₂ structures. $\langle \rangle$ denotes sample averaging.

With $F_{\text{lay}}(Q)$ the scattering amplitude for a double layer, one may write for the total scattering amplitude

$$F(Q) = F_{\text{lay}}(Q) \sum_n \left(\frac{1 + S_n}{2} + \frac{1 - S_n}{2} e^{iQ \cdot a/2} \right) e^{iQ \cdot cn} \quad (3)$$

where Q is a wave vector change of the beam, and n takes integer values, $0 < n < N$, when the scattering volume consists of a total of N double layers. Thus, after taking the sample average, $\langle \rangle$, the intensity is expressed by

$$I = NF_{\text{lay}} F_{\text{lay}}^* \left[\cos^2 \left(\frac{Q \cdot a}{4} \right) \sum_n \exp(iQ \cdot cn) + \sin^2 \left(\frac{Q \cdot a}{4} \right) \sum_n \langle S_0 S_n \rangle \exp(iQ \cdot cn) \right]. \quad (4)$$

When each layer is infinite, F_{lay} contains a term $\delta[Q - 2\pi(a^*h + b^*k)]$. The first term in (4) describes the sharp Bragg peaks (for $h = \text{even}$), whereas the diffuse lines are contained in the second term ($h = \text{odd}$). ($Q \cdot a/4 = 2\pi h/4 = \pi h/2$).

The spin correlation function may be split into two parts

$$\langle S_0 S_n \rangle = (\pm 1)^n S_a^2 + \langle s_0 s_n \rangle \quad (5)$$

where the first term contains the long-range order parameter $S_a = \langle S_n \rangle$, and the second term the fluctuation correlations. In our case we find $S_a = 0$, i.e. only short-range correlation.

The diffuse scattering from the disorder is contained in the Fourier transform of the fluctuation correlation function

$$C_n = \langle s_0 s_n \rangle. \quad (6)$$

This function is model dependent. For instance, for a first-neighbour 1D Ising case it has a form

$$C_n = c_1 D_1^{|n|}, \quad (7)$$

In a very extensive exposition of disorder in materials, Welberry (1985) shows that C_n for certain 1D cases may be expressed by a form

$$C_n = \sum_j c_j D_j^{|n|} \quad (8)$$

equivalently valid for Ising models to range j as for Markovian processes of the same range.

It turns out that a two-parameter model suffices to describe our data, leading to an intensity expression for the diffuse component of (4):

$$I_{\text{diffuse}} = |F_{\text{lay}}|^2 \{c_1 (1 - D_1^2) / [1 + D_1^2 - 2D_1 \cos(2\pi l)] + c_2 (1 - D_2^2) / [1 + D_2^2 - 2D_2 \cos(2\pi l)]\} \quad (9)$$

with l a continuous variable.

c_1 and c_2 are expressible by D_1 and D_2 and $c_1 + c_2 = 1$ (Samuelson *et al* 1991). Equivalent expressions have been derived previously in various contexts (Vainshtein 1966, Guinier 1966, Welberry 1985).

5. Data fitting and results

Observed diffuse scattering data at room temperature along $[1\bar{1}\bar{1}]$ for several samples were fitted to equation (9) by the least squares method. The parameters fitted were D_1 , D_2 and a scaling factor. The parameters c_1 and c_2 were expressed by D_1 and D_2 and were not separately fitted, thus there were up to three free parameters.

The modulating part of the diffuse lines is due to the layer structure factor $|F_{\text{lay}}|^2$. Positional parameters and temperature factors based on the structural work by Jagner *et al* (1976) were used. It was, however, found inconvenient to apply individual temperature factors, and this negligence lead to considerable disagreement with the scattering envelope. Since, however, the structural part of the problem is not the theme of the present work, this discrepancy was partly removed by reducing all z -parameters by about 15%. Some discrepancy remains, however, between the observed and the 'theoretical' layer structure factors, but this does not at all affect the fitted D_1 and D_2 values, which were obtained by fits in the 3 to 5 region of l .

In figure 5 we show the experimental and the fitted scattering profile for one particular sample, obtained with parameters

$$D_1 = 0.27 (\pm 0.02) \quad D_2 = -0.14 (\pm 0.02).$$

A close view is given in figure 6, which shows the fitted curves between $l = 2.4$ and 5.4 (Figure 6(a)), and the actual diffuse function components (figure 6(b)). One notices the two contributions corresponding to D_1 and D_2 , with their appropriate weights (0.671 and 0.329). As is seen the ' D_1 -curve' peaks at integer l -values, corresponding to the part of the correlation function containing $++$ pairs ('MDO₁-type' nearest neighbours). The ' D_2 -curve' on the contrary, peaks at half-integer l -values. It relates to the $+ -$ pairs of the correlation function ('MDO₂-type').

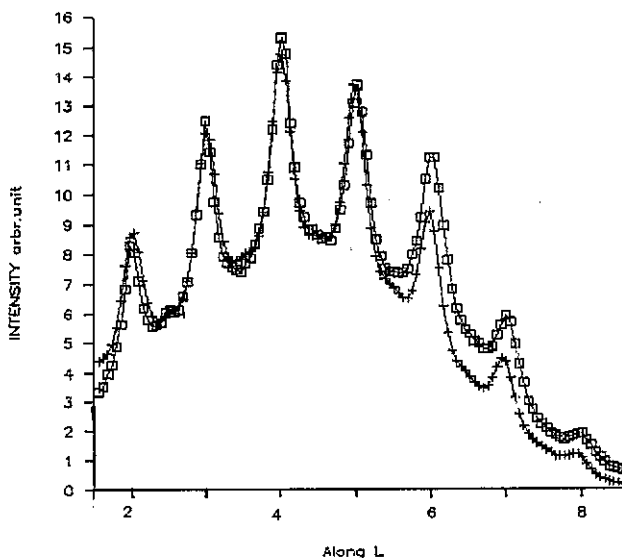


Figure 5. Diffuse scattering from DSC: observed (squares) and fitted (crosses) intensity profile along l for $[1\bar{1}1]$. The actual fitting was performed in the interval $l = (2.4-5.4)$. Deviation outside this region is due to inaccurate layer structure factors, which have not been fitted in this work (see text).

It should be noted that in our picture the two parts are not associated with particular separate regions of the sample. In the absence of true Bragg superlattice peaks, no preferred choice between the two stacking modes exists, so the average number of + and - choices are equal. The finite nearest-neighbour correlation D_1 (positive) requires a majority choice of equal-neighbour pairs, which may be both ++ and --. A positive D_1 could be caused by a 'ferromagnetic' first-neighbour coupling.

The finite next-nearest-neighbour correlation D_2 (negative) promotes, on the contrary, +- pairs. For a disordered system, a negative D_2 may be due to a ferromagnetic first-neighbour coupling, because such coupling would favour +-+- correlations irrespective of the first-neighbour coupling, while leaving the average + and - contributions equal. The peaking at half-integer indices in fact reflects the enhanced tendency of +-+ or -+- configurations in the sample.

In the succeeding paper we shall be exploring these considerations in more detail, and discuss the implication of the correlation parameters for the growth process of the DSC-crystals.

6. Raman scattering at low temperatures

Disorder in crystalline materials may also be studied by Raman scattering. In this case the disorder is revealed by broadened and/or asymmetric vibrational peaks in the lattice-vibrational part of the spectrum (Fjær and Samuelsen 1986).

In figure 7 we show observed low-frequency Raman spectra for the same sample performed at room temperature and at 50 K. The spectra are polarized with some relatively sharp and some broad lines. In particular, one notices the asymmetric feature around 80–90 cm^{-1} in the xz polarization. This feature does not change much on cooling

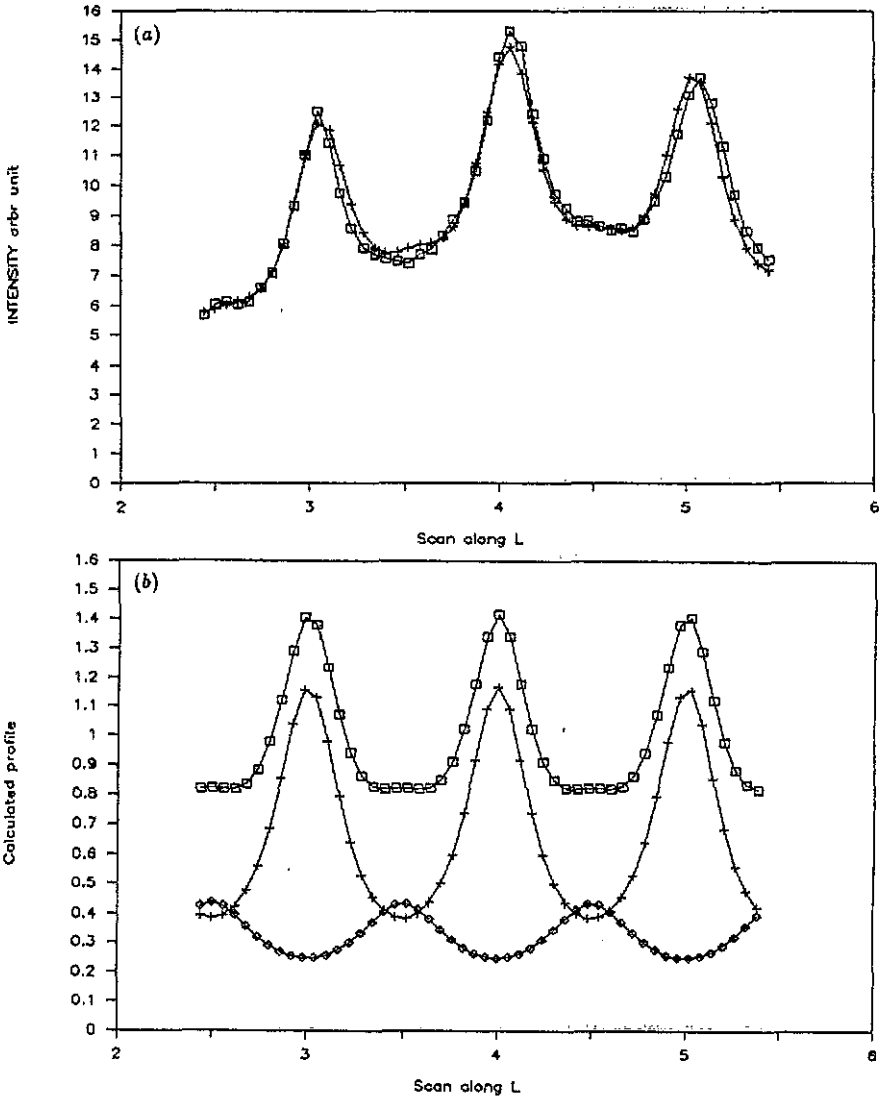


Figure 6. (a) Detailed view of observed and fitted diffuse scattering intensities from DSC along l for $[1\bar{1}l]$ (figure 5). (b) The interference function of (9) for $D_1 = 0.27$, $D_2 = -0.14$, and the contribution from each of the two terms.

to 50 K, which strongly indicates that the disorder does not change. The disorder is 'frozen in' by the growth process and is not viable for modification by cooling.

7. Conclusions

The description of order and disorder in layered materials is interesting both from a statistical physics as well as from a materials physics point of view.

Quite detailed insight can be obtained from diffraction experiments, notably the diffuse components.

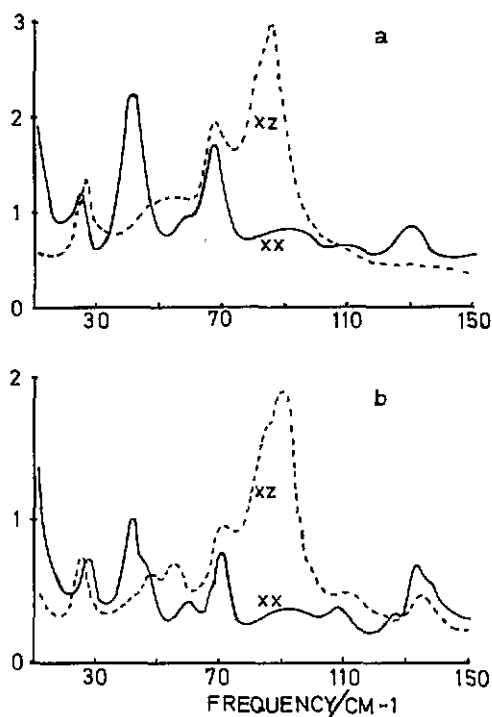


Figure 7. Raman spectra with $\lambda = 514.5$ nm taken at (a) 295 K and (b) 50 K in the lattice vibrational region between 10 and 150 cm^{-1} with polarization xx and xz .

For the present material (DSC), the detailed analyses of diffuse peak shapes and widths lead to the conclusion that short-range order exists between the few nearest-neighbouring layers (two parameter). In this picture, the sample is regarded as spatially homogeneous, as opposed to the MDO-approach, which requires spatially separate regions of two ordered phases (MDO_1 and MDO_2) and one disordered phase.

Since the diffraction pattern of DSC is characteristic for a large family of layered materials, we believe our conclusions apply quite generally. Similar experiments on other materials like $\text{K}_4\text{V}(\text{CN})_6$ will be undertaken.

In the succeeding paper (Samuelsen *et al* 1991) we discuss possible growth processes of DSC-crystals based on the short-range order description.

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