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## The Jahn–Teller effect and orientational order in $(C_nH_{2n+1}NH_3)_2CuCl_4$ , $n = 1, 2, 3$

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**Abstract.** Crystal optical and x-ray diffraction studies show that the high-temperature phase I of the perovskite-type layer compounds  $(C_nH_{2n+1}NH_3)_2CuCl_4$  with  $n = 1, 2, 3$  is Jahn–Teller distorted orthorhombic with space group  $Bbcm$  ( $D_{2h}^{18}$ ). As a consequence, the order of the  $C_nH_{2n+1}NH_3$  group leads to two configurations, realised in a monoclinic phase II with space group  $P2_1/c$  ( $C_{2h}^3$ ) and an orthorhombic phase III with  $Pbca$  ( $D_{2h}^{15}$ ). The transition sequences found above 300 K depend on  $n$ :  $I \leftarrow T_{c1} = 348 \text{ K} \rightarrow II$  for  $n = 1$ ;  $I \leftarrow T_{c1} = 364 \text{ K} \rightarrow II \leftarrow T_{c2}^h = 356 \text{ K}$ ,  $T_{c2}^e = 338 \text{ K} \rightarrow III$  for  $n = 2$ ; and  $I \leftarrow T_{c1} = 434 \text{ K} \rightarrow III$  for  $n = 3$ . The domain phenomena at  $T_{c1}$  and  $T_{c2}$  point to a subtle balance between the tilt and order configurations of phases II and III. Birefringence and lattice constants indicate a very loose inter-layer contact in phase I.

### 1. Introduction

The perovskite-type layer compounds  $(C_nH_{2n+1}NH_3)_2MCl_4$  where  $n = 1, 2, \dots$  and  $M = Mn, Fe, Cu$  and  $Cd$  show a large variety of very interesting structural phases (e.g. Kind 1980, Depmeier 1986 and references therein). Among the divalent metals  $Cu^{2+}$  is a strong Jahn–Teller (JT) ion (Reinen and Friebel 1979). Therefore, copper compounds are expected to take a special position within the whole series. Recently, the different phase sequences of  $(CH_3NH_3)_2CuCl_4$  (in short, C1Cu),  $(C_2H_5NH_3)_2CuCl_4$  (C2Cu) and  $(C_3H_7NH_3)_2CuCl_4$  (C3Cu) have been investigated mainly by optical methods (Kleemann *et al* 1979, 1983, Tello *et al* 1981, Extebarria *et al* 1988). It was presumed throughout these studies that one of the high-temperature phase transitions has to be JT-induced in each sequence. However, a clear assignment could not be made. The aim of this work is to fill this gap.

The structures consist of layers of corner-sharing  $MCl_6$  octahedra where the cavities between the octahedra are occupied from both sides by the  $NH_3$  groups of the alkylammonium (AA) chains,  $C_nH_{2n+1}NH_3$ . The N–H...Cl hydrogen bonding is weak. Adjacent layers are stacked upon one another and coupled by weak van der Waals forces between the terminal methyl groups and by long-range Coulomb interaction (Geick and Strobel 1977). In the non-JT compounds with  $n \leq 3$ , the order–disorder transitions are connected with orientational motions of the AA group as a whole. At high temperatures, the chains flip between the four equivalent states of the  $NH_3$  group in the chlorine cavity. With decreasing temperature the motion ‘freezes in’ stepwise, thus leading to various

orientational configurations of the AA chains; simultaneously, owing to the hydrogen bonding, the  $\text{MCl}_6$  octahedra are tilted and slightly distorted. Two different schemes of hydrogen bonding occur, 'aab' and 'abb' (Depmeier and Heger 1978). The letters denote the hydrogen bonds of  $\text{NH}_3$  running to axial ('a') chlorine atoms of the octahedra or to bridging ('b') chlorines in the  $\text{MCl}$  plane.

The room-temperature structures of the copper compounds with  $n = 1, 2, 3$  have been determined with the space groups  $\text{P2}_1/a$  ( $\text{C}_{2h}^5$ ) for  $\text{C1Cu}$  (Pabst *et al* 1987) and  $\text{Pbca}$  ( $\text{D}_{2h}^{15}$ ) for both  $\text{C2Cu}$  (Steadman and Willett 1970, Tichy and Depmeier 1983) and  $\text{C3Cu}$  (Barendregt and Schenk 1970). The  $\text{CuCl}_6$  octahedra are strongly distorted due to the cooperative JT effect, and the AA groups are fully ordered corresponding to the aab scheme.

The current view of the phase sequence in the JT compounds is based on the theoretical treatment by Petzelt (1975). Landau-theory arguments suggest the existence of an intermediate phase with space group  $\text{Cmca}$  ( $\text{D}_{2h}^{18}$ ) between a disordered high-temperature phase with tetragonal symmetry  $\text{I4}/\text{mmm}$  ( $\text{D}_{4h}^{17}$ ) and the room-temperature phase  $\text{Pbca}$  ( $\text{D}_{2h}^{15}$ ). In analogy to the non-JT compounds Petzelt connects the transition  $\text{I4}/\text{mmm} \leftrightarrow \text{Cmca}$  with the chain ordering, thus leaving the second transition  $\text{Cmca} \leftrightarrow \text{Pbca}$  for the JT effect. In the experiments,  $\text{C1Cu}$ ,  $\text{C2Cu}$  and  $\text{C3Cu}$  appeared as optically isotropic above  $T_{c1} = 348, 364$  and  $436$  K, respectively, and were assumed to be tetragonal, i.e. disordered and undistorted, in the high-temperature phase (Heygster and Kleemann 1977, Kleemann *et al* 1979, 1983, Tello *et al* 1981, Extebarria *et al* 1988). In addition, Tello *et al* (1981) discovered a strongly discontinuous transition in  $\text{C2Cu}$  ( $T_{c2} \approx 345$  K) and they believed it to confirm Petzelt's sequence. In a recent study, Kleemann *et al* (1983) questioned the orthorhombic symmetry of the intermediate phase in  $\text{C2Cu}$ ; contrary to Petzelt's prediction they correlated the transition at  $T_{c1}$  tentatively with the JT effect.

It was noticed by Tichy and Depmeier (1983) that the JT distortion of the chlorine octahedra is similar to the weak one occurring in the fully ordered low-temperature phases of non-JT compounds. Therefore, from an energetic point of view, one would speculate that the JT distortion should be stable far beyond the temperature region where the AA groups usually start to order. We performed optical domain observations and x-ray diffraction experiments above 300 K. Our results remove the unclear situation with regard to the JT transition and, at the same time, reconfirm the unique position of the copper compounds. A short account of the phase sequences of  $\text{C1Cu}$ ,  $\text{C2Cu}$  and  $\text{C3Cu}$  in the full temperature range has been given earlier (Jahn *et al* 1986).

## 2. Experimental details

Single crystals of  $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4$  were grown at  $40^\circ\text{C}$  by slow evaporation of a saturated aqueous solution containing stoichiometric amounts of  $\text{C}_n\text{H}_{2n+1}\text{NH}_3\text{Cl}$  and  $\text{CuCl}_2$  (Arend *et al* 1978). Special care was taken to select crystals free from mechanical deformations and liquid inclusions. The samples were dried *in vacuo* at the beginning of the experiments. Birefringence and domain formation studies were performed under the polarising microscope using an electrically heated stage. In order to prevent chemical reactions with the copper heating element and to ascertain homogeneous temperature distribution, the sample platelets were placed between two perforated platinum foils.

Precession photographs of all copper compounds were taken with graphite-monochromatised molybdenum radiation ( $\lambda$  Mo  $\text{K}_\alpha$ ). In a small cylindrical heating device the

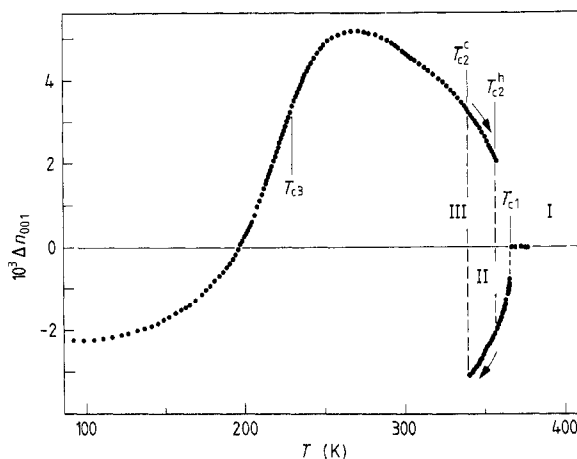


Figure 1. Linear optical birefringence of C2Cu as a function of temperature ( $\lambda = 633$  nm).

crystal plate ( $2 \times 2 \times 0.3$  mm<sup>3</sup>) was fixed free of stress between  $7.5$   $\mu$ m thick Kapton foils. A copper shield with Kapton windows kept the temperature inhomogeneity to less than 1 K within the illuminated part of the sample. The temperature homogeneity within the furnace and the calibration of the thermocouples could be checked very easily by observing the phase transitions under the polarising microscope. In the same way, domain effects and crystal quality were scrutinised during the measurements.

The lattice constants of C2Cu were measured on a focusing single-crystal diffractometer (Knorr 1985). Temperature variation between 40 and 370 K was performed by means of a closed-cycle refrigerator combined with a heating device. The absolute value of  $T$  was correct within 1 K, the stability better than 0.1 K. The absolute values of the lattice constants for the orthorhombic room-temperature phase,  $a = 7.49$  Å,  $b = 7.38$  Å and  $c = 21.27$  Å, were obtained by Guinier powder diffraction with Si as reference material. In order to facilitate the comparison between the different phases, the direction of the crystallographic axes will be retained even if a non-standard setting for a space group results.

### 3. Crystal optics

#### 3.1. Birefringence

In the room-temperature phase of C2Cu, denoted by phase III, we determined the relation between the main refractive indices along the orthorhombic axes  $a$ ,  $b$  ( $<a$ ) and  $c$ :  $n_b > n_a > n_c$ . Numerical values for the refractive indices have been given by Kleemann *et al* (1983). In a heating run, the birefringence of an ideal virgin (001) plate,  $\Delta n_{001} = n_b - n_a$ , abruptly changes sign at 356 K ( $= T_{c2}^h$ ); on cooling the reverse happens around 338 K ( $= T_{c2}^c$ ). This behaviour is shown in figure 1 (Jahn 1976). The slight waviness of the curve is caused by multiple beam interference in the anisotropic crystal (Bosch *et al* 1986). Birefringence switching and hysteresis width clearly indicate that the phase transition into the intermediate phase II is strongly of first order. Within the coexistence region,  $|\Delta n_{001}(T)|$  has nearly the same value in both phases. The maximum difference at  $T_{c2}^c$ ,  $|\Delta n^{III}| - |\Delta n^{II}| \approx 10^{-4}$ , is in agreement with Kleemann *et al* (1983). The values of  $T_{c2}^{h,c}$  depend on the sample quality (§ 3.2). A weakly discontinuous transition into the high-temperature phase I occurs at 364 K ( $= T_{c1}$ ). Above, the birefringence is zero

within an uncertainty of about  $5 \times 10^{-5}$ . C2Cu looks optically uniaxial. We mention that the high-temperature transition of C3Cu is of first order, too (Holocher 1986, Holocher *et al* 1989). Extebarria *et al* (1988) find a continuous transition. Birefringence measurements down to 10 K gave no hints for a phase transition of the type II  $\leftrightarrow$  III in C1Cu and C3Cu.

### 3.2. Domain observations

The copper compounds are more stable against mechanically induced twinning than others (Arend *et al* 1978). An explanation in which way the JT effect is involved has not been given so far. We studied the twin formation in C2Cu at 300 K,  $T_{c1}$  and  $T_{c2}$ . Supposing C2Cu is ferroelastic in phase III, a compressive twin formation should be expected for a uniaxial pressure applied along the  $a$  axis ( $a > b$ ). Unfortunately, the softness of the material prevents this experiment. However, cutting the mono-domain plates perpendicular to [110], for example, induces a pattern of strip domains with the walls parallel to [110] and/or  $[\bar{1}\bar{1}0]$ . This pattern is due to twinning as verified by x-rays in § 4.2. It is important to note that the stress-induced twins of phase III as well as the domains of phase II and III (around  $T_{c2}$ ) differ in their crystal optics in the same way: the index ellipsoids appear to be rotated by  $90^\circ \pm \delta$  against each other around [001]. At 300 K,  $\delta$  amounts to  $1.5^\circ$  for twins of phase III; at  $T_{c2}$ ,  $\delta \approx 1^\circ$  for domains of the phases III and II. Therefore, the stress-induced twins and the domains of different phases of C2Cu cannot be distinguished under the polarising microscope. Kleemann *et al* (1983) measured the temperature-dependent  $\delta$  between  $T_{c2}$  and  $T_{c1}$ . They explained the non-zero  $\delta$ -value by a lower symmetry than orthorhombic for phase II. In § 4.2 we will give another explanation.

Formation and movement of twin walls can be controlled in some way by application of a shear stress in the (001) plane combined with a small uniaxial pressure parallel to [001]. Technically, the crystal platelets ( $\sim 50 \mu\text{m}$  thick) were kept between parallel glass plates and the stress was exerted by hand. The resulting twin pattern depends on the shear stress direction. In a virgin sample, [100] stress induces walls parallel to both [110] and  $[\bar{1}\bar{1}0]$  directions, whereas [110] stress induces only [110] walls. The twin formation starts with extremely fine needles at the surface, their cross section being wedge-shaped with an acute angle of about  $4^\circ$ . With increasing stress the wedge grows through the crystal plate. Reversal of the shear stress direction reverses the direction of the wall movement, and the stress-induced twin component can be made to disappear fully. In some cases, a large part of the sample could be switched reversibly between both indicatrix orientations. The twin walls can be also moved by a shear stress perpendicular to the wall direction in the layer. In this case, saw-tooth-shaped twin boundaries develop with twin walls meeting under an angle of about  $2^\circ$ .

The domain phenomena occurring at  $T_{c1}$  have been studied by Heygster and Kleemann (1977). Remarkably, the domains appearing on cooling were found to be restricted to a small temperature range only; below  $T_{c1} - 3$  K, the crystal was in the mono-domain state again. This transient domain formation has been explained by a twinning process as usual for a transition between a tetragonal and a lower-symmetry phase. We studied a series of thin platelets around 364 K. In really ideal crystals there is no domain formation in either a cooling or a heating run. In slightly strained samples strip domains occur; their stability range below  $T_{c1}$  (ranging between 0.1 and 1 K) seems to be strain-dependent. There is one important feature that has been overlooked in earlier work: in all crystals, whether they show this transient domain formation or not, the indicatrix

orientation of the resulting mono-domain below  $T_{c1}$  is always identical to that of the initial mono-domain sample in phase II. Such a clear preference could not be understood in the case of tetragonal symmetry of phase I. The doubts are supported by the analogous behaviour of C1Cu and C3Cu, where the mono-domains obtained below  $T_{c1}$  get back the orientation of their initial room-temperature state.

A very complex situation arises in strained C2Cu crystals around  $T_{c2}$ . For a sample showing only a few needle-shaped domains at 300 K, two steps in entering phase II can be followed. First, the needles, originally the second twin component of phase III, increase their width continuously without changing their indicatrix orientation; this process starts near  $T_{c2}^c$ . In the next step, the less strained main parts of the sample switch spontaneously at temperatures near  $T_{c2}^h$ . Sometimes, the domains of both processes coalesce. Often thin needles with the indicatrix orientation of the first twin component of phase III survive up to  $T_{c1}$ , decreasing their width with increasing  $T$ . On cooling, the process II  $\rightarrow$  III proceeds in an analogous manner. Defining  $T_{c2}^{h,c}$  as the temperatures where the main part of the sample switches on heating and cooling, respectively, the hysteresis width is found to vary between 10 and 23 K in strained crystals. In a strongly stress-twinned sample, the room-temperature pattern looks essentially stable up to  $T_{c1}$ , and only small changes occur around  $T_{c2}$ . At  $T_{c1}$ , the bright domain pattern disappears, but very weak residuals of the pattern can be followed up to 20 K beyond  $T_{c1}$ . Upon cooling, the number of needle-shaped domains appears to decrease below  $T_{c1}$ .

## 4. X-ray diffraction

### 4.1. Space groups

Precession photographs were made for the different phases of C1Cu, C2Cu and C3Cu, respectively. In each case the reciprocal ( $a^*$ ,  $b^*$ ) plane for  $l = 0, 1, 2$  was recorded. Domain phenomena were excluded by optical inspection. We obtain the following correspondences:

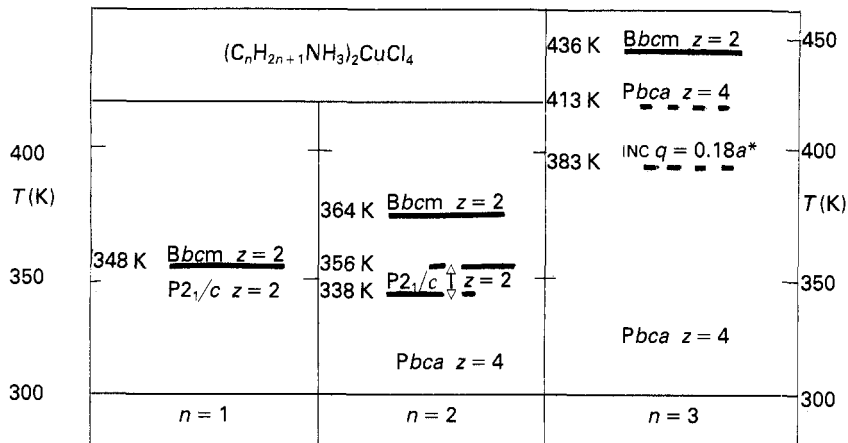
- (i) the high-temperature phases of all compounds are identical (phase I);
- (ii) the room-temperature phase of C1Cu agrees with the intermediate phase of C2Cu (phase II);
- (iii) the room-temperature phases of C2Cu and C3Cu are identical (phase III).

The reflection conditions of phase III are in agreement with those expected for space group  $Pbca$  (Steadman and Willett 1970, Barendregt and Schenk 1970). The important result is that phase I is clearly not tetragonal. The sharp Bragg reflections follow the conditions:

$$hkl: h + l = 2n \quad 0kl: k, l = 2n \quad h0l: h, l = 2n \quad hk0: h = 2n.$$

With the reasonable assumption that the point group  $mmm$  of phase III is preserved, the space group of phase I becomes  $Bbcm$  (standard setting  $Cmca$  ( $D_{2h}^{18}$ )). The unit cells of both phases are identical. The essential change in going from III to I is the appearance of a new mirror plane within the perovskite-type layers. The primitive cell of phase I containing two formula units is monoclinic with  $b$  as the monoclinic axis.

The integral reflection condition found for phase II is identical to that for I. Additional conditions observed for  $h0l: h, l = 2n$  and  $0k0: k = 2n$  lead to the monoclinic non-conventional space group  $B2_1/a$  or  $B2_1/c$ . A comparison with space group  $Bbcm$  shows that the  $c$  glide plane is preserved at the transition I  $\leftrightarrow$  II. Therefore, the space group



**Figure 2.** High-temperature phase sequences of  $(C_nH_{2n+1}NH_3)_2CuCl_4$ . The number of formula units,  $z$ , is given for the primitive unit cell.

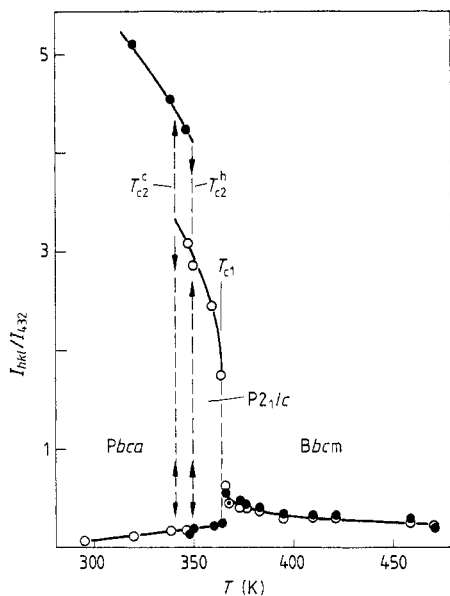
$P2_1/c$  ( $C_{2h}^5$ ) is chosen. The transformation is achieved by  $a'_{II} = (a_{II} - c_{II})/2$ ,  $b'_{II} = b_{II}$  and  $c'_{II} = c_{II}$  where the unprimed symbols are in  $B2_1/c$ . Very recently, Pabst *et al* (1987) reported the equivalent space group  $P2_1/a$  for the room-temperature phase of  $C1Cu$ .

In figure 2 the transition sequences of  $C1Cu$ ,  $C2Cu$  and  $C3Cu$  above 300 K are given. Phase II ( $P2_1/c$ ) is not realised in  $C3Cu$ . Instead we find an incommensurate (INC) phase within phase III with  $Pbca$  (Holocher 1986, Jahn *et al* 1986). The modulation-vector behaviour is nearly identical to that of the phase  $\gamma$  in  $(C_3H_7NH_3)_2MnCl_4$  (Depmeier 1981). The situation in the manganese compound has been studied by Murlt (1986). Details on  $C3Cu$  will be given shortly (Holocher *et al* 1989).

In  $C2Cu$  we studied the stability range of phase II and the switching between phases II and III in more detail. Precession photographs of  $(hk2)$  were taken up to 470 K. Around 450 K,  $C2Cu$  starts to decompose. Space group  $Bbcm$  could be followed up to the highest temperature. Figure 3 shows the temperature dependence of the integral intensities of the strong reflections 302 and 032 (orthorhombic setting). The primary beam instabilities were corrected by using the Bragg reflection 432. In phase I the diffuse intensities of 302 and 032 coincide within the accuracy obtained; they increase when approaching  $T_{c1}$ . The step in the Bragg intensities at  $T_{c2}$  is caused by the 30% intensity increase of the 432 reflection in phase II. With a correction, the intensities of 302 and 032 would fit together smoothly.

#### 4.2. Twin and phase boundaries

In order to verify the compressive twin formation at 300 K, the  $(hk0)$  plane of strained  $C2Cu$  and  $C3Cu$  samples was recorded. The additional reflections found point towards a second twin component of phase III. The twin reflections are transformed into each other by a  $(110)$  or  $(1\bar{1}0)$  mirror plane indicating that the twin walls are parallel to these directions. The angle between the crystallographic  $a$  or  $b$  axes of these twins deviates slightly from  $90^\circ$ . Heating the strained sample to 20 K beyond  $T_{c1}$  did not change the intensity ratio of the twin reflections. This clearly shows that the twin domains generated at 300 K by elastic stress are in fact due to the second twin component of the orthorhombic high-temperature phase I. The consequences of the 'Jahn-Teller twins' for the twinning



**Figure 3.** Reduced integral intensities of the reflections ●, 302 and ○, 032 (monoclinic setting: §02 and 132, respectively) of the phases of C2Cu.

at  $T_{c1}$  and  $T_{c2}$  will be discussed in § 5.2. Remarkably, after cooling to room temperature the stress-generated twin component was strongly suppressed. We note that the reflection pattern of the  $(hkl)$  planes with  $l = 0, 1, 2$  cannot give any information on whether domains of phase II are also contained in a stress-twinned sample.

We studied a C2Cu sample with domains of phases II and III coexisting at 340 K. Again, the reflections of the  $(hk2)$  plane show that the phase boundaries are parallel to  $[110]$  or  $[\bar{1}\bar{1}0]$  and the angles between the crystallographic  $b$  axes of neighbouring domains are  $90^\circ \pm \delta$ . In both cases of  $\pi$ T twins and phase coexistence, the canting angle is found to be a function of the ratio  $a/b$ , with the temperature dependence given by

$$\delta(T) = |90^\circ - 2\arctan[a(T)/b(T)]|.$$

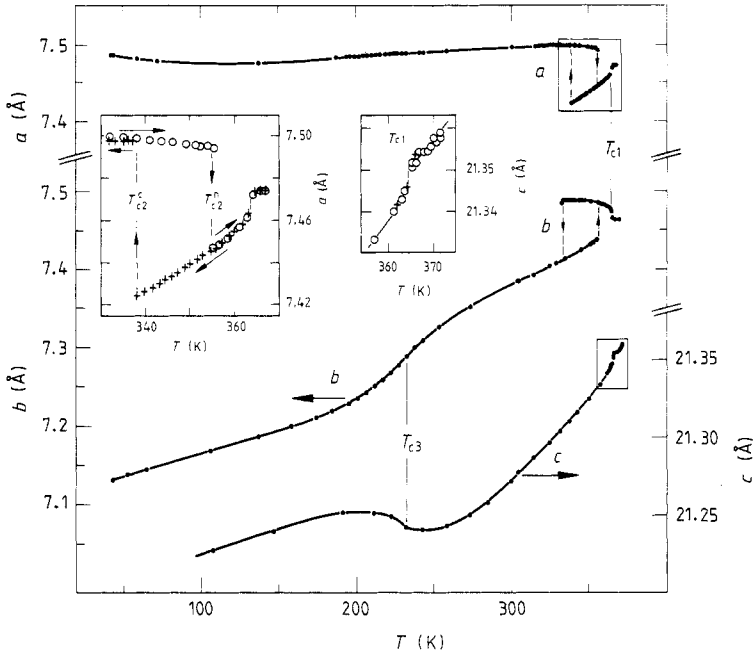
The  $\delta(T)$  values obtained by optics and x-rays are in full agreement with calculations using the experimental lattice constants determined in the next section.

#### 4.3. Lattice constants of C2Cu

In a preliminary measurement, a C2Cu sample glued on a Be plate did not show the  $T_{c2}$  transition at all. We therefore fixed the platelet free of stress between Kapton foils. The intensities of the reflections 400, 040 and 0012 were fitted by a Gaussian function, and from the temperature-dependent line shifts relative to the 300 K position the lattice constants  $a$ ,  $b$  and  $c$  were calculated. In figure 4 the orthorhombic setting is used, since the monoclinic distortion in phase II is expected to be small. In the room-temperature phase of C1Cu, the monoclinic angle deviates from the corresponding orthorhombic value by less than  $0.5^\circ$  (Pabst *et al* 1987).

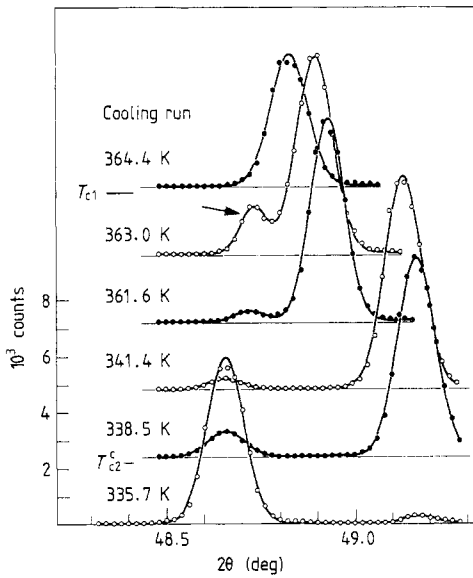
At  $T_{c1}$ , all lattice constants change discontinuously. In phase I,  $a$  and  $b$  are equal within the experimental error,  $(a - b) = (0.008 \pm 0.012) \text{ \AA}$  at 366 K. The measurement of  $b$ , performed after that of the constant  $a$ , gave a 5 K lower value for  $T_{c2}^c$ . We believe that the cycling runs within the whole temperature range induced strain fields that tend to stabilise phase II on cooling. In the case of  $c$ , the possible discontinuity at  $T_{c2}$  should be smaller than  $0.003 \text{ \AA}$ . Therefore, a change of the cell volume must be very small at





**Figure 4.** Temperature dependence of the lattice constants of C2Cu. The insets give details of  $a$  and  $c$  around  $T_{c1}$ : ●, heating; +, cooling.

this transition. Below 300 K, the lattice constants of C2Cu have been measured by neutron diffraction (Tichy *et al* 1983). The agreement with our data is good. The constants  $b$  and  $c$  behave anomalously around 232 K. Preliminary Guinier powder data indicate a triclinic symmetry below  $T_{c3}$ .



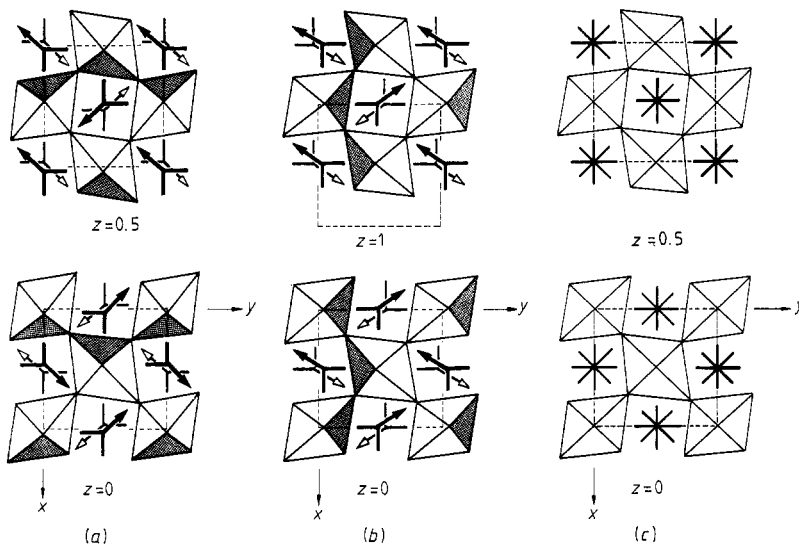
**Figure 5.** Integral intensity of the 400 reflection (orthorhombic setting) of C2Cu during the transitions I  $\rightarrow$  II and II  $\rightarrow$  III.

Figure 5 shows the intensity of the 400 reflection during a cooling run. The transient domain phenomenon studied in § 3.2 manifests itself in an additional reflection immediately below  $T_{c1}$  (arrow in figure 5). A weak residual of this reflection survives down to  $T_{c2}^c$  where the 400 of phase III grows at the same  $2\theta$  value. Below  $T_{c2}^c$ , a very weak peak remains at the position of the 400 of phase II which could be followed down to 320 K. The additional peaks point either to twinning of the  $\pi$  type or to domains of coexisting phases II and III, induced and stabilised by elastic strains in both cases. A definite answer cannot be given from these data. In the case of twinning, the coinciding reflections 400 and 040 of the components reduce the difference  $(a - b)$  to  $0.001 \pm 0.004 \text{ \AA}$  at 366 K.

## 5. Discussion

### 5.1. Relation between phases III, II and I

First the room-temperature structure (phase III) of C2Cu (Steadman and Willett 1970, Tichy and Depmeier 1983) and C3Cu (Barendregt and Schenk 1970) is considered. Figure 6(a) schematically shows the layers projected onto the (001) plane at  $z = 0$  and  $z = \frac{1}{2}$ , respectively. The long Cu–Cl bonds ( $\sim 3.0 \text{ \AA}$ ) of the distorted  $CuCl_6$  octahedra are in the copper–chlorine plane; the short in-plane Cu–Cl distances and the axial bond lengths are nearly equal ( $\sim 2.3 \text{ \AA}$ ). The characteristic long-axes alignment is uniform in the (010) plane and zig-zag in (100). In figure 6, the orientational order of the alkylammonium groups is characterised by the N–H . . . Cl hydrogen bonds (triangles). The arrows mark the bonds running to the bridging chlorines. The AA groups above and below the plane are transformed into each other by a centre of inversion. The octahedra are tilted due to the interaction with the  $NH_3$  groups, and the tilt axes are nearly parallel to  $y$  in phase III. This leads to a washboard-like puckering of the octahedron layers. At 300 K the tilt angle is about  $6.5^\circ$ .



**Figure 6.** Schematic representation of the alkylammonium group configuration and octahedron tilt pattern in the phases III (a), II (b) and I (c).

The room-temperature structure of C1Cu (phase II) as determined by Pabst *et al* (1987) is given in figure 6(b). The unit cell (broken lines) belongs to space group  $P2_1/a$ . In phase II, the tilt-axis direction is nearly parallel to the  $x$  axis. At 300 K, the JT distortion and even the tilt angle correspond to those in phase III.

The essential new symmetry element of the high-temperature phase I is the mirror plane within the perovskite layer. Therefore, the AA groups have to be disordered. The orthorhombic symmetry indicates that the octahedra are still statically distorted by the JT effect. As the result, we expect the time- and space-averaged structure given in figure 6(c). The octahedra are untilted. We see now that phases II and III follow directly from the fact that the AA chains order in an orthorhombic matrix. In the non-JT methyl compounds, the symmetry reduces from  $I4/mmm$  to  $Abma$  ( $Cmca$ ) (Knorr *et al* 1974); then, two twin components are allowed with the octahedron tilt axes being perpendicular to each other. In the copper compounds, however, the two tilt-axis directions are no longer equivalent: instead of twins one gets two crystallographically different structures. Besides the tilt-axis direction they differ also in their AA group orientational pattern: the hydrogen bonds, aligned parallel in the (010) plane of phase II, are anti-parallel in phase III. Obviously, phase III allows a closer packing in the case of the long hydrocarbon chains.

The structure of C2Cu in phase II has not been determined so far. We point out that a second AA group configuration generated by (100) mirror planes would also be compatible with  $P2_1/c$ . However, in this hypothetical configuration all AA groups would have to reorientate at the transition  $II \leftrightarrow III$  whereas only half do in the pattern of C1Cu (figures 5(a) and (b)). We propose therefore the C1Cu pattern for the intermediate phase of C2Cu, too.

The space groups of the ordered phases II and III,  $P2_1/c$  and  $Pbca$ , are both maximal non-isomorphic subgroups of the high-temperature space group  $Bbcm$ : the phase transition  $Bbcm \rightarrow P2_1/c$  is 'translationengleich',  $Bbcm \rightarrow Pbca$  'klassengleich', with the index 2 in either case (*International Tables for Crystallography* 1983). This means that considering only the number of symmetry elements—including the translation vectors—which are lost at the phase transitions, the strongly discontinuous transition  $P2_1/c \rightarrow Pbca$  of C2Cu is not connected with an increase of symmetry. The space groups of C3Cu are part of the predicted sequence by Petzelt (1975) where the possibility of a Landau-type transition has been investigated. The most exciting feature is the subtle balance between the different ordering schemes. In the case of C2Cu, this is documented by the strongly strain-dependent  $T_{c2}$ , by a negligible volume change at  $T_{c2}$  and by the diffuse intensities of the 032 and 302 reflections which show the same temperature dependence above  $T_{c1}$  (figure 3).

### 5.2. Jahn–Teller twins and the twinning at $T_{c1}$

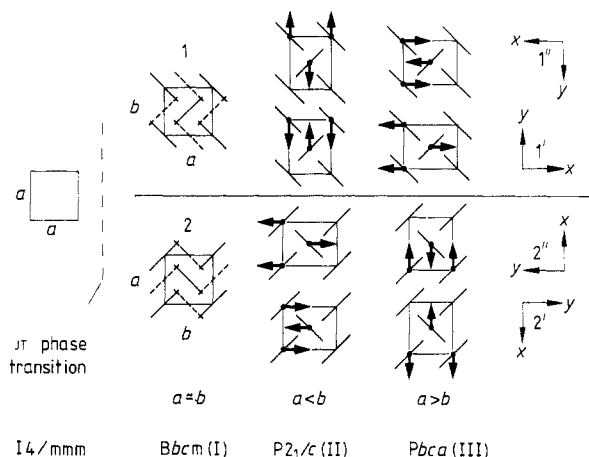
In principle, the static JT distortion of the octahedra provides for an additional degree of freedom in stacking the layers along [001]: shifting the  $z = 0$  layer in figure 6(a) by  $(a + b)/2$  switches the long-axis zig-zag pattern from (010) into (100). Both unit cells are transformed into each other by a  $90^\circ$  rotation around [001]. Normally, twins of this type ('JT twins') should occur at the JT phase transition itself where the octahedron distortions become long-range correlated. In the copper compounds, the tetragonal phase with probable space group  $I4/mmm$  is not accessible. However, the twins generated by external stress are exactly of the JT type. Since the two twin components are switched into each other by reversing the shear-stress direction, the generating mechanism cannot

be a slip process. During the switching, the in-plane Cu–Cl bonds of the octahedra have to exchange their lengths every second layer; simultaneously the tilt-axis direction rotates by  $90^\circ$  and a reorientation of the AA chains takes place. Evidently, the energy needed for the generation of JT twins is much higher than that needed for the twin generation in the non-JT compounds. Figure 7 schematically shows the JT-twin components 1 and 2 of phase I and the twins  $1'$ ,  $1''$  and  $2'$ ,  $2''$  emerging from these during the order–disorder phase transitions, respectively. For simplicity, only the long axes of the octahedra projected onto (001) have been drawn. The octahedral tilt pattern of the  $z = 0$  layer is indicated by the shift directions of the (upper) axial chlorine atoms. The AA groups have been omitted.

The twin domains occurring at a phase transition are related by the symmetry operations which are lost (Wondratschek and Jeitschko 1976). At  $I \rightarrow II$ , the twinning planes are (100) and (001). Therefore, (010) crystal sections should be used in a microscopic study on the formation of twins  $1'$ ,  $1''$  or  $2'$ ,  $2''$  in phase II. At the transition  $I \rightarrow III$ , only anti-phase domains are allowed ( $III, 1'$  and  $III, 1''$ , for example) which cannot be distinguished by linear crystal optics. This means that the twins of phase II have to disappear at the transition  $II \rightarrow III$ . As the result, the transient domain phenomenon observed on (001) plates at  $T_{c1}$  cannot be explained by twinning due to the AA group order in the orthorhombic matrix. Instead, the phenomenon has to be caused either by JT twins of phase II or by coexisting domains of II and III belonging to one twin component. In both cases the distortion energy would be reduced at the phase transition. An argument in favour of the second possibility might be drawn from the delicately balanced competing interactions present in this system. Domains of phases II and III preserve the symmetry of phase I. In addition, during the formation of JT twins half of the layers would have to switch their octahedral long-axis directions at  $T_{c1}$ .

### 5.3. Zero in-plane birefringence

The unusual phenomenon that an orthorhombic or lower-symmetry crystal behaves optically uniaxial even occurs twice in the copper compounds; however, the physical mechanisms are different. At low temperatures, wavelength-dependent ‘isotropic’



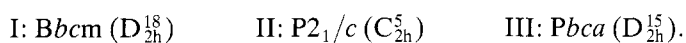
**Figure 7.** Jahn–Teller twin components (1, 2) of phase I and the resulting twins ( $1'$ ,  $1''$ ,  $2'$ ,  $2''$ ) of the phases II and III (schematically).

points have been found in C1Cu (Will 1983) and C2Cu (Fernandez *et al* 1985). In C2Cu (figure 1),  $\Delta n(195 \text{ K}) = 0$  for  $\lambda = 633 \text{ nm}$ . It has been shown by Willett *et al* (1974) that many copper (II) chloride complexes undergo thermochromic phase transitions. The dispersion anomaly is due to changes of the coordination geometry in the  $\text{CuCl}_4^{2-}$  anions. Obviously, these structural changes are not necessarily connected with a phase transition. In C1Cu, the dispersion anomaly starts at 200 K though the crystal structure remains monoclinic between 300 and 100 K (Pabst *et al* 1987). In C2Cu, on the other hand, there is a symmetry reduction at 232 K; the anomalous behaviour of  $\Delta n(T)$  and of the lattice constants  $b$  and  $c$  arising about 50 K above  $T_{c3}$  looks like the short-range order effect at a continuous phase transition.

The zero in-plane birefringence above  $T_{c1}$  is common to C1Cu, C2Cu and C3Cu. One possible reason, namely an equal distribution of JT twins along  $z$ , has to be ruled out. In the classical theory of birefringence (Born and Huang 1954), the optical anisotropy is due to anisotropic local dipole fields acting on the electric point dipoles which are induced at each lattice site. In principle, the local dipole fields have to contain the contributions from the atoms of the whole crystal. Consequently, the zero in-plane birefringence of the orthorhombic copper compounds may be either a fortuitous result of the octahedral stacking geometry or a strong indication that the disordered crystals are an arrangement of isolated layers. In the latter, each layer approaches four-fold symmetry. Then the orthorhombic crystal structure can be built up by using four-fold screw axes as symmetry operations, whereby the screw axes parallel to  $[001]$  are thought to be located at  $x = \frac{1}{4}$ ,  $y = \frac{1}{4}$  in figure 6(c): adjacent layers along  $z$  are alternately related by either a local  $4_1$  or  $4_3$  axis. As the transmission of light through crystals is described by a (centro-symmetric) second-rank tensor, the local screw axes act as a macroscopic four-fold rotation axis.

## 6. Conclusions

In spite of efforts in the past, the macroscopic methods led to the wrong space-group assignments for the high-temperature phases of  $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4$  with  $n = 1, 2, 3$ . Instead of the theoretically predicted (Petzelt 1975) and experimentally adopted phase sequence,  $I4/mmm (D_{4h}^{17}) \leftrightarrow \text{Cmca} (D_{2h}^{18}) \leftrightarrow \text{Pbca} (D_{2h}^{15})$ , the copper compounds undergo structural transitions between the following phases:



In a first view, Petzelt's intermediate phase  $D_{2h}^{18}$  looks identical to that actually found for the high-temperature phase I of all copper compounds; however, in disagreement with his assumption the orthorhombic symmetry is caused by the JT effect and not by the orientational order of the alkylammonium groups. The thermal decomposition prevents the copper compounds from reaching the undistorted tetragonal phase. The orthorhombic matrix allows two different tilt-order configurations in the ordered state. Which one of these structures is realised depends on the length of the hydrocarbon chain. Whereas the compounds with  $n = 1$  and 3 exhibit either of them, both structures are stable in C2Cu.

The different phase sequences may be explained phenomenologically by using the concept of competing interactions (Cowley 1980). One has to introduce two inter-layer interactions, either favouring one of the two tilt and order systems. Their strength will be influenced by the constituents of the alkylammonium chains and, eventually, by several external parameters. We mention that birefringence measurements on the fully

deuterated methyl compound,  $(CD_3ND_3)_2CuCl_4$ , give a markedly reduced discontinuity at  $T_{c1}$  as compared with  $C1Cu$  (Will 1983). This result is of interest in a discussion on how the competing interactions can be modified in order to get multi-critical points in these compounds. The non-JT compounds without competing interactions show normal critical behaviour at their high-temperature transition (Knorr *et al* 1974).

The equal lattice constants  $a$  and  $b$  as well as the zero in-plane birefringence both point to a very loose inter-layer contact above  $T_{c1}$ . It is an interesting question whether a compressive twin formation could also be performed in phase I. Some information on whether the character of the JT transition would be really two-dimensional could be gained from studying the positional disorder of the octahedron layers along the stacking axis. The crystals for this experiment would have to be grown in phase I and kept strictly at temperatures above  $T_{c1}$ .

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