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An Anomalous Reversible Phase Transformation in α-Dichlorobis(pyridine)cobalt(II) Near 150 K

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Crystallographic methods have been used to examine the low-temperature phase transformation occurring at about 150 K between the α- and γ-forms of dichlorobis(pyridine)cobalt(II). The reversible transformation is characterized by unusual thermal hysteresis in the magnetic anisotropy [Bentley, Gerloch, Lewis & Quested, *J. Chem. Soc.* (*A*), (1971). p. 3751], and is also unusual in that the low-temperature polymorph has the higher symmetry. The crystallographic transition exhibits thermal hysteresis of at least 5 ± 1 K, and whilst the occurrence of the down-temperature transition is dependent on the rate of change of temperature, the reverse transition is not. The phase transformation may involve abrupt repositioning of complete polymeric chains of dichlorobis(pyridine)cobalt(II) without any intermediate stages.

Introduction

Three crystalline modifications of dichlorobis(pyridine)cobalt(II), hereinafter COPYCL, are known within the temperature range 89 to 400 K. These are the polymeric octahedrally coordinated α-form, first prepared by Reitzenstein (1894), the monomeric tetrahedrally coordinated β-form, prepared by Hantzsch (1927), and the recently discovered polymeric octahedrally coordinated γ-form (Clarke & Milledge, 1975). The β- and γ-forms may both be obtained from α-COPYCL *via* reactions occurring in the solid state, β-COPYCL by heating to 390 K in a sealed tube (Cox, Shorter, Wardlaw & Way, 1937; Wendlandt, 1965), and γ-COPYCL by cooling to about 150 K (Bentley, 1968; Thomas, 1969). Only the α- and γ-forms show a close structural relationship because of the radical change in the cobalt coordination on transformation to β-COPYCL.

Bentley, Gerloch, Lewis & Quested (1971) measured the principal and mean magnetic susceptibilities of α-COPYCL in the temperature range 300–80 K, and found that at about 150 K the anisotropy in the *ab* plane abruptly changed sign. In addition, the anisotropy in both the *ab* and *bc* planes exhibited a thermal hysteresis loop extending from 148 to 160·5 K.

We have examined, by crystallographic methods, the interconversion of α- and γ-COPYCL at low temperature in order to elucidate the origin of the unusual hysteresis found by Bentley *et al.* (1971) in the magnetic anisotropy of α-COPYCL in the region of the phase transformation. All of the crystallographic experiments were performed on the low-temperature X-ray camera of Thomas (1972) with crystals mounted in thin-walled glass tubes. Changes in X-ray diffraction pattern during cooling of the specimen may be easily monitored in the low-temperature camera by the so called skid-oscillation method in which an oscillation photograph is taken whilst the film is translated at a known rate parallel to the camera rotation axis. The temperature corresponding to any point on the resultant smeared-out reflexions may be deduced from the distance swept out by the reflexions since the start of the experiment and a temperature/time graph. The technique may therefore be used in either a qualitative way to search for abrupt changes in Bragg angles or in a semi-quantitative way to estimate the temperature at which such changes occur.

Although temperatures indicated by the thermocouple may be measured to a precision of ±0·5 K, Thomas (1969) has shown that a correction factor of 2·5 ± 2 K must be added to the indicated temperature in order to obtain readings on an absolute scale. The correction factor arises because design limitations necessitate the positioning of the thermocouple measurement junction approximately 1 cm away from the specimen although the two are thermally linked by 1 mm diameter high conductivity copper wire, and by an atmosphere of helium gas at 10 mm Hg pressure. In principle, therefore, temperature differences may be measured more accurately than absolute temperatures.

Application of the skid oscillation method to α-COPYCL (Thomas, 1969) revealed an abrupt change in the Bragg angles at about 130 K when the temperature was decreasing and 150 K as the temperature was increased. This hysteresis in the crystallographic transformation from α- to γ-COPYCL was therefore akin to that in the magnetic anisotropy, although the extent of the hysteresis loop was considerably smaller for the magnetic results.

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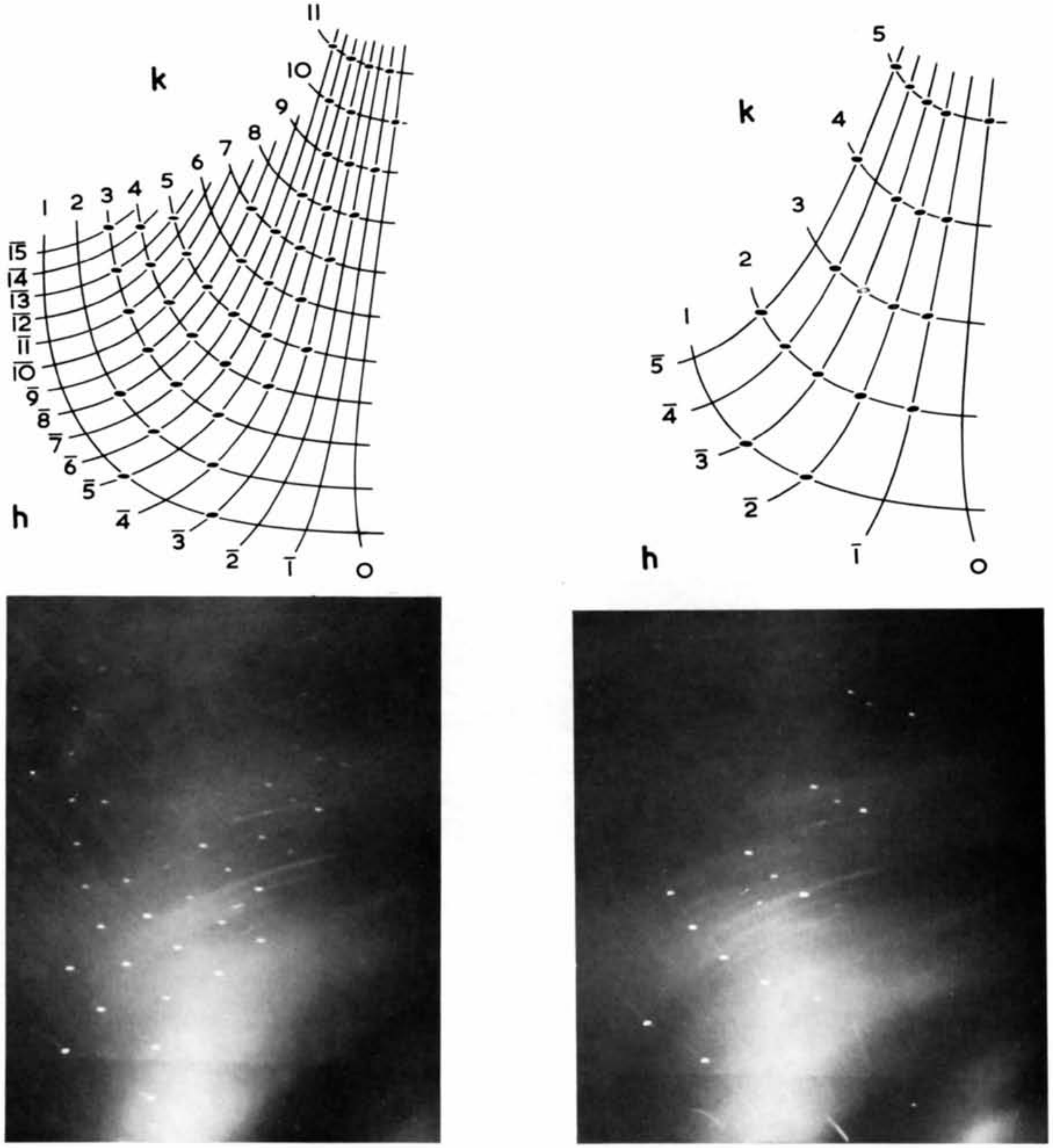

(a) (b)

Fig. 1. Normal beam $hk1$ Weissenberg photographs and corresponding festoon patterns. (a) α-COPYCL (294 K), (b) γ-COPYCL (89 K).

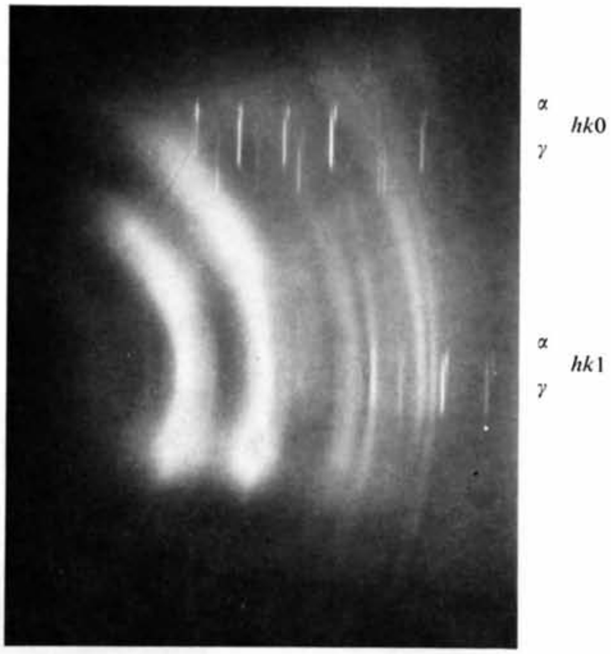

Fig. 3. Skid oscillation photograph taken whilst passing slowly through the transition from γ- to α-COPYCL. The temperature range swept out is 149·5 to 153·0 K.

Physical effects of the phase transformation

The onset of the phase transformation from α- to γ-COPYCL is characterized by violent agitation of the whole crystal which in several cases led to complete fragmentation. Frequently the resultant crystal of γ-COPYCL was split into two or more pieces. In general, crystal splitting was reduced by use of cooling rates less than 0·2 K min^{-1} in the region of the transition, but even so only one undamaged crystal of γ-COPYCL was obtained in 31 attempts. The incidence of crystal splitting was greatest for the first transformation suffered by the crystal, but obviously the ease with which it occurred was a great hindrance to experimental work. Particularly rapid cooling such as that produced by a gas flow cooling apparatus of the type described by Post, Schwartz & Fankuchen (1951) induced such violent tremors that the crystal was dislodged from its mounting, and cartwheeled along the surrounding glass tube. It would therefore appear that considerable mechanical strain builds up within the crystal as it approaches the transformation temperature and is released during the transition.

The symmetry and unit cells of α-and γ-COPYCL

The systematic absences and space groups given in Table 1 were derived from *hk*0, *hk*1, and *hk*2 Weissenberg photographs of α- and γ-COPYCL. Comparison of *hk*1 and *hk*2 photographs revealed that festoons of reflexions with *h* and *k* odd in the diffraction pattern of α-COPYCL had disappeared on transformation to γ-COPYCL (Fig. 1), indicating that the *a* and *b* axes of γ-COPYCL were approximately half the length of those of the α-form. Long exposure Weissenberg photographs of γ-COPYCL did not reveal extra reflexions corresponding to a super lattice, and there is therefore a genuine halving of the *a* and *b* axes during the transformation. The *hk*0 Weissenberg photographs of α- and γ-COPYCL are very similar however because the space-group absences for α-COPYCL dictate that only reflexions with *h* and *k* even appear in this zone. The high-angle triplet reflexions, characteristic of twinning in α-COPYCL (Clarke & Milledge, 1975), reverted to the more usual α_1–α_2 doublet reflexions in γ-COPYCL, crystals of which had complete single-crystal character.

Photographs of crystals returned to room temperature after transformation to γ-COPYCL were the same as those taken before the cooling cycle showing that the α/γ-COPYCL transformation was completely reversible. In the two cases where direct comparison was possible, it also appeared that the reversibility extended to the triplet reflexions, which arise through twinning in α-COPYCL, since the ratio of the three intensities composing the triplet was the same before and after the cooling cycle. This result indicates that, even after transformation to γ-COPYCL, there is still an inherent difference between the crystal domains corresponding to different α-COPYCL twins, but

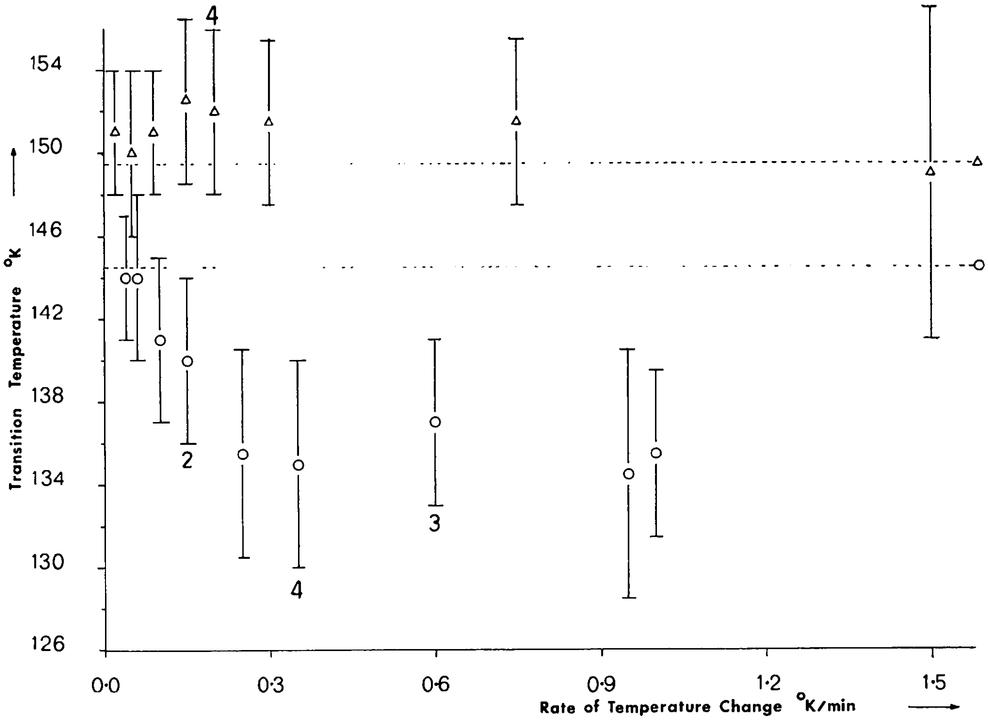

Fig. 2. Transition temperature (K) for the α/γ-COPYCL transition *vs.* rate of change of temperature (K min^{-1}). Δ temperature rising; ○ temperature falling. Dotted lines represent limiting values from constant temperature experiments (see text). Numbered points are for crystals other than crystal 1 (Table 3).

Table 1. *Systematic absences and space-group data for α- and γ-COPYCL*

	α-COPYCL	γ-COPYCL
Absences		
hkl	$h+k=2n+1$	none
$0kl$	$(k=2n+1)$	none
$h0l$	$(h=2n+1)$	$h+l=2n+1$
$hk0$	(h), $k=2n+1$	none
$h00$	$h\neq4n$*	$(h=2n+1)$
$0k0$	$k\neq4n$*	$k=2n+1$
$00l$	none	$(l=2n+1)$
Space group	$C2/b$ (c unique)	$P2_1/n$ (b unique)
Z	8	2

* Not a space group condition.

further experimental work is required to establish the reliability of this indication.

α- and γ-COPYCL are monoclinic with space groups $C2/b$ (c unique), and $P2_1/n$ (b unique) respectively, but α-COPYCL has lower symmetry than γ-COPYCL and a larger unit cell and asymmetric unit. In structural terms this lower symmetry means that only alternate layers are crystallographically equivalent in α-COPYCL, whereas all layers are crystallographically equivalent in γ-COPYCL. The occurrence of the higher symmetry polymorph at low temperature in a system related by a displacive phase transformation is a most unusual result. Indeed, the high-temperature polymorph so frequently has the higher symmetry that this condition is included by Buerger (1951) in his list of characteristics of displacive phase transformations. Because of the reversal of the symmetry criterion, the α/γ-COPYCL transition also contradicts another of Buerger's rules, namely that the down-temperature transformation almost invariably results in twins, but, in accord with Buerger's criterion, it is the lower symmetry α-COPYCL which exhibits twinning.

In order to clarify the relation between the unit cells of α- and γ-COPYCL, the unit-cell parameters were determined at various temperatures by a least-squares fit to Bragg angles measured by the Van Arkel method (Henry, Lipson & Wooster, 1960, p. 172) with Cu $K\alpha$ radiation (α_1 1·54051 Å; α_2 1·54433 Å). The length of the c axis and the angle β were determined in this way only at the two lowest temperatures, and the room-temperature cell parameters were derived from Bragg angles measured by the Straumanis method (Henry *et al.*, 1960) with Co $K\alpha$ radiation (α_1 1·78892 Å; α_2 1·79278 Å). The results of these measurements are given in Table 2.

Both the a and b axes of α-COPYCL contract smoothly on cooling from room temperature to 152·5 K, the mean coefficients of thermal expansion in this temperature range being $2{\cdot}55\times10^{-5}$ K^{-1} and $2{\cdot}33\times10^{-5}$ K^{-1} respectively, but there is no significant change in the monoclinic cell angle γ. Between 152·5 K and 145·5 K, the a and b axes are halved in length from 34·46 and 17·34 Å to 17·45 and 8·416 Å respectively, and the unique axis changes from c to b. In terms of the α-COPYCL unit cell, these changes represent an expansion of the a axis by 0·54 Å ($34{\cdot}46-2\times17{\cdot}45$) and a contraction of the b axis by 0·51 Å ($17{\cdot}34-2\times8{\cdot}416$). The expansion along the a axis is one source of the mechanical strain which develops during the transition. Analysis of the crystal structures of α- and γ-COPYCL (Clarke & Milledge, 1975) reveals that the changes in the lengths of the a and b axes are due to rotation about the c axis of half of the polymeric chains in the structure. Below 145·5 K, the a and b axes of γ-COPYCL again contract smoothly with mean coefficients of expansion of $1{\cdot}4\times10^{-5}$ K^{-1} and $1{\cdot}7\times10^{-5}$ K^{-1} respectively. The smaller expansion coefficients for γ-COPYCL reflect the 52 Å^3 decrease in the volume of the α-COPYCL unit cell as a result of the transition.

Unfortunately, the experimental data are not extensive enough to allow definitive comment on the occurrence, or otherwise, of anomalous expansion in the region of the transition. The four experimental points for α-COPYCL certainly yield a linear relationship within experimental error between the unit-cell volume and temperature, but the three points for γ-COPYCL are inconclusive since the experimentally determined unit-cell volume at 121·5 K [$\frac{1}{4}\times2122{\cdot}4$ (56) Å^3] is only one standard deviation greater than the value of $\frac{1}{4}\times2117{\cdot}0$ Å^3 required to produce a perfect linear relationship over the three points.

The transition temperature

Previous work on the transition temperature and hysteris range for the α/γ-COPYCL transition has left unanswered the question of the variation of these

Table 2. *Cell parameters for α- and γ-COPYCL at various temperatures*

Form	T(K)	a (Å)	b (Å)	c (Å)	β or γ (°)	V (Å^3)
γ	89·0	17·437 (13)	8·408 (2)	3·593 (7)	90·05 (5)	$\frac{1}{4}\times$ 2107·2 (88)
γ	121·5	17·446 (9)	8·412 (1)	3·615 (7)	90·08 (3)	$\frac{1}{4}\times$ 2122·4 (56)
γ	145·5	17·451 (3)	8·416 (1)	3·61 (1)†	90·07*	$\frac{1}{4}\times$ 2123·6 (72)
α	152·5	34·363 (1)	17·343 (2)	3·65 (1)†	90·135 (8)	2175·2 (65)
α	198·5	34·379 (4)	17·377 (2)	3·65 (1)†	90·137 (9)	2180·5 (66)
α	237·5	34·402 (1)	17·385 (1)	3·66 (1)†	90·138 (7)	2188·9 (66)
α	294·0	34·486 (3)	17·408 (2)	3·6635 (6)	90·121 (6)	2199·3 (12)

* Not refined by least-squares calculations.
† Measured from oscillation photographs.

quantities with the number of times a particular specimen had been transformed and the rate of temperature change near the transition point. Accordingly, we have used the skid oscillation method to search for such variations using twinned crystals of α-COPYCL. The results of such measurements are given in Table 3 and Fig. 2, and show that the transition temperature is independent of the number of times the specimen has been transformed. The limited data available also indicate that the transition temperature does not vary significantly from specimen to specimen, a conclusion partially confirmed by a mean estimate of 152·5 ± 2 K for the upward transition temperature using a 10 mg sample in the Perkin Elmer differential scanning calorimeter (DSC II). There is, however, a definite trend toward a decrease of the downward transition temperature with increased cooling rate, although the upward transition temperature shows no such variation. These observations are consistent with the fact that domains of γ-COPYCL, which has a unit-cell volume 2·4% smaller than that of α-COPYCL, could be tolerated within a surrounding matrix of the α-form, but the reverse situation would not occur readily since it would require severe compression of the α-COPYCL domains.

Table 3. *The variation of the temperature of the α/γ-COPYCL transition*

Crystal	Number of transformations	Rate of change of temperature (K min^{-1})	Transition temperature (K)
(*a*) Temperature falling			
1	15	0·04	144·0 (30)
1	21	0·06	144·0 (40)
2	1	0·10	141·0 (40)
1	9	0·15	140·0 (40)
1	7	0·25	135·5 (40)
4	1	0·35	135·0 (50)
3	1	0·60	137·0 (40)
1	17	0·95	134·5 (60)
1	3	1·00	135·5 (40)
(*b*) Temperature rising			
1	20	0·02	151·0 (30)
1	12	0·05	150·0 (40)
1	18	0·09	151·0 (30)
4	2	0·20	152·0 (40)
1	4	0·30	151·5 (40)
1	14	0·30	152·5 (40)
1	2	0·75	151·5 (40)
1	8	1·50	149·0 (80)

The skid oscillation data in Table 3 yield a limiting value for the thermal hysteresis of 6 ± 8 K, a rather unsatisfactory result because of the large experimental error which arises through errors in measuring the films due to the low resolution of the termini of the integrated reflexions, and through errors in temperature calibration. At rates of change of temperature less than 0·06 K min^{-1} estimation of the transition temperature was further complicated by the overlap of the reflexions from the two polymorphs in the temperature ranges 150–155 K for the upward transition, and 145–141 K for the downward transition (Fig. 3). The cause of this phenomenon is discussed in the following section.

The existence of genuine hysteresis of at least 5 ± 1 K was, however, confirmed using constant temperature experiments. A crystal of α-COPYCL was cooled to 144·5 ± 0·5 °K and maintained at this temperature for 160 min without undergoing transformation. The crystal was cooled further until it transformed to γ-COPYCL and then heated slowly to 149·5 ± 0·5 K. The γ-COPYCL crystal was maintained at this temperature for 230 min, also without undergoing transformation. The minimum value of the hysteresis is considerably less than those of 20 and 12·5 K obtained in previous studies (Thomas, 1969; Bentley *et al.*, 1971) but these authors give no indication of the rates of change of temperature used in their work. The transition temperatures obtained in the magnetic studies are about 10 K higher than those determined here, but this may simply arise from the differences in the design of the apparatus employed in the two investigations. In both sets of apparatus, the thermocouple measurement junction is placed at some distance from the specimen, and, as noted previously, this can lead to systematic errors in absolute temperature measurements. Nevertheless, it seems clear that the hysteresis loop in the magnetic anisotropy of α-COPYCL is a direct result of the hysteresis in the phase transition between α- and γ-COPYCL.

Discussion of the mechanism of the transformation

The interpretation of diffuse scattering has proved a powerful method for studying the molecular processes involved in phase transformations and solid-state reactions (Lonsdale, Nave & Stephens, 1966; Welberry, 1973) especially where these processes involve the disruption of the normal periodic properties of the crystal lattice. In order to extract information about solid-state reactions from X-ray diffraction photographs it is of course necessary to distinguish between diffuse scattering due to short-range order and that due to thermal motion (Flack, 1970; Glazer, 1970). Laue photographs of α- and γ-COPYCL in the region of the phase transformation, taken with white + Cu $K\alpha$ radiation, and a maximum exposure of 100 min, exhibit no diffuse scattering at all and certainly no dramatic effects of the kind investigated by Welberry (1973) using the same equipment. Further, the diffuse scattering of α-COPYCL is rather weak even at room temperature and conforms to that expected from a chain structure as a result of thermal vibration (Lonsdale, 1942). The lack of diffuse scattering associated with the α/γ-COPYCL phase transformation indicates that either there are no intermediate stages involving short-range order or loss of periodicity, or that such stages are so short lived as to be undetectable on the time scale of the X-ray experiment. The latter possibility seems unlikely in view of the coexistence of the two forms discussed in the following paragraph.

Skid oscillation photographs taken at low rates of change of temperature indicate coexistence of the two polymorphs, since reflexions from both forms appear side by side on the film over a 5 K temperature range (Fig. 3). As the temperature is slowly changed, the reflexions of one polymorph gradually weaken in intensity whilst those of the other grow stronger, but the two are clearly separated in Bragg angle because of the large difference in cell parameters and do not merge into one another. Zubov (1956) has shown that the rate of the phase transformation between α- and β-quartz may be controlled by manipulation of the thermal gradient within the specimen, and that partly transformed samples may be preserved indefinitely by this means. It is possible that the coexistence of α- and γ-COPYCL is also a manifestation of the thermal gradient within the specimen, since the phenomenon is only apparent when low rates of change of temperature, and hence small thermal gradients, are employed. In any case, the definite angular separation of the reflexions from the two polymorphs implies an abrupt change in cell parameters at the transition rather than a gradual shift from one to the other.

The presence in both α- and γ-COPYCL of polymeric chains linked by Co–Cl bonds suggests that the integrity of these chains is preserved during the phase transformation. This view is supported by the fact that the α/β-COPYCL transformation, which requires disruption of these chains, does not occur until the α-form is heated to almost 400 K. We are therefore led to the conclusion that the phase transformation between α- and γ-COPYCL must involve abrupt repositioning of complete polymeric chains of COPYCL. The results of the crystal structure analyses presented in the previous paper show that the majority of this movement occurs in the direction of the chain length, but that some repositioning also takes place in the plane normal to this. In both structures, the only contact between neighbouring polymeric chains of COPYCL is *via* the pyridine rings which make van der Waals contacts on all sides. Relative movement of the polymeric chains along their length would require complete rows of pyridine rings to slide past each other to their new positions, and clearly there would be a considerable energy barrier to this process. Presumably, the forces promoting the transition would gradually build up until they just overcame the energy barrier, at which point the transformation would occur instantaneously.

Sudden reorganization of the crystal structure in this way would certainly explain the frequent occurrence of crystal shattering at the transformation, and the existence of an energy barrier would account for the dependence of the downward transition temperature on the cooling rate and also explain the hysteresis. At the downward transition, energy is being removed from the crystal by cooling, whereas to surmount the energy barrier the crystal must acquire energy. There is therefore a tendency, which increases with increased cooling rate, to overshoot the transformation point, and a sufficiently great cooling rate may result in the well known phenomenon of quenching of the high-temperature phase. The upward transition temperature is relatively independent of the heating rate since the energy to overcome the barrier is always being supplied. The thermal hysteresis in the transition has a similar source to the dependence of the downward transition temperature on cooling rate. In order to build up the potential energy created by the chains pushing against each other to an extent sufficient to overcome the energy barrier to the downward transformation, the crystal must be cooled to a temperature lower than that of the upward transition.

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