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The Structure of the High-Temperature α-Modification of $Cs_2PbCu(NO_2)_6$ and the Jahn–Teller Induced α → β-Phase Transition—A Neutron Diffraction Study

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Copper–lead nitrocomplexes exhibit multistage transitions between phases, which are characterized by static, planar dynamic and three-dimensionally dynamic Jahn–Teller effects, respectively. In this study the structure of the cubic high-temperature α-modification of $Cs_2PbCu(NO_2)_6$ and the nature of the $\alpha \rightleftharpoons \beta$-phase transition is investigated by neutron diffraction.

1. Introduction

The study of lead nitrocomplexes $A_2PbCu(NO_2)_6$ [A: Cs, Rb, Tl, K] by EPR spectroscopy yields multistage phase transitions which for the cesium compound take place at the following temperatures (*1–3*):

$$\begin{array}{ccccccc} \gamma & T_{c1} & \beta' & T_{c2} & \beta & T_{c3} & \alpha \\ \text{monocl.} & \underset{275^\circ\text{K}}{\overset{289^\circ\text{K}}{\rightleftarrows}} & \text{o-rhomb.} & \underset{294^\circ\text{K}}{\overset{310^\circ\text{K}}{\rightleftarrows}} & \text{o-rhomb.} & \underset{381^\circ\text{K}}{\overset{391^\circ\text{K}}{\rightleftarrows}} & \text{cubic} \end{array}$$

The low-temperature γ-modification contains tetragonally elongated CuN_6 octahedra—possibly with an orthorhombic component—in antiferrodistortive order, as could be deduced from spectroscopic experiments (*3*). All attempts have failed so far to grow untwinned single crystals of this phase for neutron diffraction structural analysis. However, X-ray powder diagrams at 275°K showed distinct splittings of the 222 and 440 reflections (*1*) and—in agreement with a structural study of γ-$K_2PbCu(NO_2)_6$ single crystals (4)—indicated monoclinic symmetry. We finally performed high resolution neutron powder experiments at 160°K with the D1A instrument in Grenoble. The results (*6*) confirm the antiferrodistortive model (*1–3*), which is suggested for γ-$K_2PbCu(NO_2)_6$ also (*4*).

According to results of spectroscopic measurements, the β′-phase of $Cs_2PbCu(NO_2)_6$, which is nearly identical with the β-modification, is characterized by the essentially two-dimensional Jahn–Teller dynamics in the (001)-planes of the o-rhombic lattice, leading to an equilibration of the long and short Cu–N distances normal to the [001]-direction (*2*, *3*). A neutron diffraction investigation yielded tetragonally compressed CuN_6 octahedra with anomalous N and O temperature ellipsoids in the Cu–N bond directions of the (001)-plane (*5*), which is in agreement with the proposed mechanism of a planar dynamics.

In this study the Jahn–Teller induced phase transition from the o-rhombic β-modification (a = 11.04(1) Å; b = 11.01(1) Å; c = 10.74(1)

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Å) into the cubic α-phase and the structure of the α-phase will be investigated.

2. Experimental Details and Results

Several $CsPbCu(NO_2)_6$ crystals were studied by means of neutron diffraction, from which all the larger species turned out to be polycrystalline. Finally, a small crystal of 1.3 mm^3 volume proved to be useful and was measured with the P49 four-circuit diffractometer of the FR2 reactor Karlsruhe. However, in the β-phase two twin components were found for this crystal also, in addition to the dominating one. The dominating component 1 leads to the twins 2 and 3 by mirroring on the (011) and $(01\bar{1})$ plane and a successive rotation by 90° around the c_2- and c_3- axis, respectively (Fig. 1). The ratio of measured intensities of equivalent reflections of these three components is 100:36:8. When heating beyond T_{c3} the intensities vary, and also the Bragg angles of reflections of the dominating component undergo slight changes while the intensities of reflections of the medium and weak components decrease to zero. For this reason the transition from the orthorhombic β-phase to the cubic α-phase was studied more thoroughly on a strong reflection of the medium component. The (080)-plane of this component was brought into the reflecting position and the specimen temperature varied. Between 298°K, and up to 392°K, the intensity of this reflection remained constant within the statistical error. Between 392 and 398°K the measured intensity dropped to the background measuring rate. In this range the temperature was increased by increments of 1°K[1] and the integral intensities of the reflection were determined by ω-scanning. These intensities have been entered as circles in Fig. 2. The corresponding intensities of the cooling process, which were also measured by ω-scanning, are represented by crosses. Obviously a hysteresis is present because the α → β-phase transition takes place between 396 and 390°K now. After cooling below 390°K the position of the reflection agreed well with its position prior to heating. However, its integral intensity was 10% above the value before heating up. Therefore, in Fig. 2 the values obtained during the cooling process were normalized to the values obtained for the heating process. Repeated transitions from the orthorhombic β-phase into the cubic α-phase and back into the orthorhombic β-phase yielded the following findings:

After slow or fast phase transitions from the α- into the β-phase and vice versa three orthorhombic components were found.

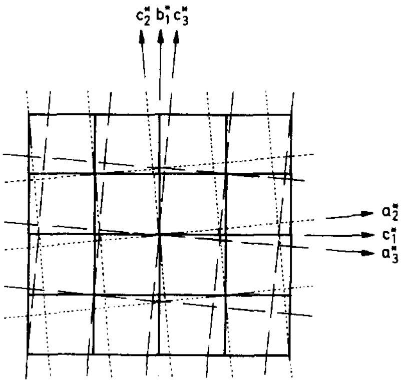

FIG. 1. The three components of the orthorhombic β-phase of a $Cs_2PbCu(NO_2)_6$ crystal ($\mathbf{a}_1^* \| \mathbf{b}_2^* \| \mathbf{b}_3^*$).

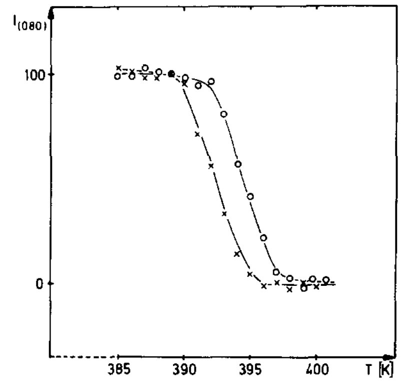

FIG. 2. Integral intensities of the (080)-reflection of the medium size domain within the temperature range of the $\beta\text{-} \underset{390°K}{\overset{398°K}{\rightleftharpoons}} \alpha$-phase transition.

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[1] While the measured temperatures with respect to one another are correct within ±0.1°K, the absolute error may come up to ±3°K.

The intensity ratios of equivalent reflections of the three components were subject to variations. However, these variations were always such that the dominating, the medium, and the weak components kept their identities.

Figure 2 confirms the results provided by EPR spectroscopy, i.e., that the $\alpha \rightarrow \beta$-phase transition is a first-order event (*2*). The transition temperatures are in fair agreement with those found by thermoanalysis [DSC: 388.5 and 393.5°K (*7*)] and polarization microscopy [387.5 and 393.5°K (*8*)] and about 8° higher than those observed by single-crystal EPR spectroscopy [381 and 391°K (*2*)]. Another interesting feature is that the same domain structure and comparable extensions of the domain areas were observed in EPR spectroscopy (*9*) as with neutron diffraction. Also by polarization microscopy twinnings can be observed parallel to the rhombic dodecahedron faces $\{01\bar{1}\}$ (*8*).

The cubic α-structure was determined by compiling the measured data using an automatic STOE four-circle diffractometer. The rules of extinction confirm the space group *Fm*3 already proposed for the cubic structures of $K_2PbCu(NO_2)_6$ (*10–12*) and of $Tl_2PbCu(NO_2)_6$ at room temperature (*12*). At 420 ± 2°K the intensities of 257 reflections with $\sin \theta/\lambda < 0.5$ Å^{-1} were recorded by ω-scanning in an octant of the reciprocal space. Taking the average of the symmetrically equivalent reflections (*hkl*, *lhk*, *klh*) 86 symmetry-independent reflections resulted. Starting with the parameters of the orthorhombic β'-phase (*5*) and using isotropic temperature factors for Cs, Pb, and Cu, which were constructed by averaging over the positional parameters of the three N- and the three O-atoms, we refined by the least-squares method. We obtained the parameters collected in Table I and an R-value of 0.068 according to $R_I = (\sum |I^{\mathrm{obs}} - I^{\mathrm{calc}}|)/\sum I^{\mathrm{obs}}$. All reflections were taken into account in this calculation. Leaving aside the reflections with $F^{\mathrm{obs}} < 3\sigma(F)$ the R-value was: $R_F = (\sum ||F^{\mathrm{obs}}| - |F^{\mathrm{calc}}||)/\sum |F^{\mathrm{obs}}| = 0.041$. The unit cell dimensions and local parameters yielded the bond lengths

TABLE I

ATOMIC PARAMETERS OF α-$Cs_2PbCu(NO_2)_6$ IN *Fm*3

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cs	0.25	0.25	0.25	0.39(8)	0.39(8)	0.39(8)	0	0	0
Pb	0	0	0.5	0.19(9)	0.19(9)	0.19(9)	0	0	0
Cu	0	0	0	0.41(9)	0.41(9)	0.41(9)	0	0	0
N	0	0	0.1981(4)	0.27(4)	0.53(5)	0.49(4)	0	0	0
O	0	0.0968(5)	0.2612(6)	0.79(5)	0.49(4)	0.56(5)	0	0	0.01

TABLE II

INTERATOMIC DISTANCES (Å) AND ANGLES IN CUBIC[a] COMPOUNDS $A_2PbCu(NO_2)_6$

A	Cs[b,c]	Cs[a,b] (*5*)	K[b] (*10*)	K (*11*)	K (*12*)	Tl (*12*)
Cu–N	2.174(7)	2.177(7)	2.114(5)	2.111(4)	2.118(2)	2.118(6)
Pb–O	2.826(9)	2.855(9)	2.794(5)	2.793(3)	2.778(1)	2.802(3)
A–O	3.219(9)	3.217(4)	3.116(5)	3.106(1)	3.116(2)	3.135(2)
N–O	1.267(8)	1.242(9)	1.224(5)	1.260(4)	1.247(2)	1.252(4)
∢ONO (deg)	113.8(9)	116.7(9)	118.2(1)	117.9(4)	116.9(2)	116.6(5)

[a] Averaged bond lengths in o-rhomb. β'-phase.

[b] Neutron diffraction.

[c] This study (420°K).

TABLE III

ROOT MEAN SQUARE DISPLACEMENTS (Å) OF N- AND O-ATOMS IN $A_2CuPb(NO_2)_6$

A	$Cs^{a,b}$	$Cs^{a,c}$ (5)		K^a (10)	K (11)
N	0.13(1)	0.11(1)	0.15(1)	0.176(10)	0.166(5)
	$0.18(1)^e$	$0.16(1)^e$	$0.15(1)^e$	$0.163(4)^e$	$0.166(5)^e$
	$0.17(1)^d$	$0.13(1)^d$	$0.22(1)^d$	$0.175(10)^d$	$0.198(5)^d$
O	0.22(1)	0.17(1)	0.19(1)	0.232(4)	0.251(5)
	$0.17(1)^e$	$0.14(1)^e$	$0.15(1)^e$	$0.167(5)^e$	0.159(3)
	$0.19(1)^d$	$0.17(1)^f$	$0.23(1)^d$	$0.203(4)^d$	0.213(4)

[a] Neutron diffraction.

[b] This study (420°K).

[c] o-rhomb. β′-phase (293°K) left: N- and O-atoms ‖ [001] (static); right: in (001)-plane (2-dimensional dynamics) (5).

[d] In or (approximately) parallel to Cu–N bond directions.

[e] Perpendicular to *d*(*f*) in the plane of the NO_2-ligands.

[f] Approximately in N–O bond directions.

and angles listed in Table II. They are compared with literature data for other cubic lead copper nitrocomplexes.

The unit cell dimension is $a = 10.97(2)$ Å, which means that it slightly exceeds the value of the mean lattice constant found for the orthorhombic β′-phase (10.93(1) Å; 293°K) (*5*). The larger Cu–N bond lengths compared to the K- and Tl-compounds (Table II) are expected on the basis of data from ligand field (*1*) and Mössbauer spectroscopy (*13*) and can be attributed to the geometric influence of the lattice expanding Cs^+ ion. The relatively small ONO bond angle is conspicuous. The rms displacements of Cs^+, Pb^{2+}, and Cu^{2+} have values within the usual range: 0.15(1) Å, 0.11(1) Å; 0.16(1) Å (*5, 10, 11*). The respective values for the N- and O-atoms are on an average 0.17 and 0.20 Å, respectively (Table III, columns 1, 3–5). They are significantly larger than the values of 0.13 and 0.16 Å, which are observed for a static distortion [Table III, column 2; cf. also (*14*)]. This result can be interpreted as indicative of a three-dimensionally dynamic Jahn–Teller effect. It was predicted by Dunitz and Orgel (*15*) already and confirmed by model calculations (*11*). More striking is the increase in the thermal parameters of the N- and O-atoms in or parallel to the Cu–N bond directions, going from the static to the dynamic phase, however, though it is less distinct than for the transition to the two-dimensional dynamics (Fig. 3; Table III, columns 2 → 1,4,5 and 2 → 3). It is remarkable with the O-atoms that the longest axis of the thermal ellipsoids runs always normal to the plane of the NO_2 ligands. Obviously, the vibrational torsion mode par-

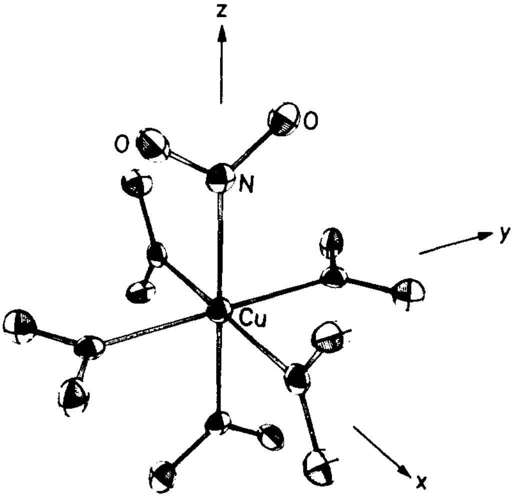

FIG. 3. The $Cu(NO_2)_6$-polyhedra in cubic α-$Cs_2PbCu(NO_2)_6$.

ticipates with an unusually high degree in the thermal movement of these groups.

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