monoclinic angle of the low-temperature phase for α-NiNSal is smaller than for α-CuNSal (see Table 2). α-PdNSal has the strongest steric interactions and exists only in the monoclinic phase.

Besides the steric interactions between the structure-building elements (the rigid molecule stacks) there are other factors influencing the transition temperatures, such as the different atomic masses of Ni and Cu on the one hand and of Pd on the other, or the fact that there exists an $s = \frac{1}{2}$ spin system for the Cu^{II} compound (Bartowski & Morosin, 1972).

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References

ADLHART, W. & SYAL, V. K. (1981). *Z. Kristallogr.* **154**, 227–233.
BARTOWSKI, R. R. & MOROSIN, B. (1972). *Phys. Rev. B*, **6**, 4209–4212.
HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
ROBERTS, P. & SHELDRICK, G. M. (1976). *XANADU*. Univ. of Cambridge, England.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.
SHELDRICK, G. M. (1976). *SHELX*. A program for crystal structure determination. Univ. of Cambridge, England.
STEURER, W. & ADLHART, W. (1983*a*). *Acta Cryst.* B**39**, 344–349.
STEURER, W. & ADLHART, W. (1983*b*). *Acta Cryst.* B**39**, 349–355.

Acta Cryst. (1983). B**39**, 721–724

The Structure of the Incommensurate Modulated Phase of α-Bis(*N*-methylsalicylaldiminato)copper(II)*

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Abstract

The modulated structure of the title compound [α-CuNSal, $Cu(C_8H_8NO)_2$] was determined at 270 K by single-crystal X-ray methods. The refinements were performed in the superspace group P^{Ibca2}_{111} (α00) considering fluctuations in phase and amplitude, respectively, of the static modulation wave. Final overall R factors $R = 0{\cdot}176$ and $R_w = 0{\cdot}065$ were obtained for 8338 independent reflexions (with $I > 0$) including 3542 first- and 3046 second-order satellite reflexions. The modulation waves are sinusoidal with main displacements parallel to **c** and small longitudinal components parallel to **a**. The phason factors were found to be comparable to the normal Debye–Waller factors with high values for the atoms around the central Cu^{II} ion and small values for the peripheral atoms, thus showing the same tendency as the amplitudes. The results are comparable to those for the isotypic modulated structure of the corresponding Ni compound.

Introduction

Recently the incommensurate modulated structure of α-CuNSal [305 (2) > T > 241 (2) K] has been the subject of a study (Adlhart, Blank & Jagodzinski, 1982) in which the authors explained the intense diffuse scattering around the satellite reflexions by phase fluctuations of the static displacement wave. In order to obtain reliable proof for this assumption from the Bragg reflexions, a refinement of the modulated structure taking into account a phason factor was performed in a similar way as for the isotypic modulated structure of α-NiNSal (Steurer & Adlhart, 1983*a*; hereafter referred to as part I).

Experimental

The preparation of the crystal, the modus of data collecting and the data reduction were described in Steurer & Adlhart (1983*b*; part II hereafter).

20 542 reflexions out of 26 992 measured main, first- and second-order satellite reflexions had intensities greater than zero and were classified as observed. Considering anomalous dispersion the equations

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$|F(hklm)| = |F(\bar{h}klm)| = |F(h\bar{k}lm)| = |F(\bar{h}\bar{k}lm)|$ and $|F(hkl\bar{m})| = |F(\bar{h}kl\bar{m})| = |F(h\bar{k}l\bar{m})| = |F(\bar{h}\bar{k}l\bar{m})|$ are valid. After averaging, 8338 reflexions remained.

Structure refinement

The modulated phase shows sharp satellites of first- and second-order beside the main reflexions. The wavevector $\mathbf{q} = 0{\cdot}297\ (4)\ \mathbf{a}^*$.

Strong satellites can be observed in all layers except $l = 0$ where only very weak satellites can be found. Therefore the atomic displacements must essentially take place along **c** with only small components parallel to **a** and **b**. The same considerations are valid for the dynamical displacements causing the diffuse scattering (see Adlhart *et al.*, 1982).

Using the (3 + 1)-dimensional superspace group approach of de Wolff, Janssen & Janner (1981) we can derive from the extinction rules *hklm*: $h + k + l = 2n + 1$, *h*0*lm*: $h = 2n + 1$ and 0*kl*0: $k = 2n + 1$ centering *I* and the symmetry elements $(^{a}_{1})$ and $(^{b}_{1})$. Therefore we have the Bravais class P^{Immm}_{111} and the superspace group $P^{Ibca2}_{11\bar{1}}$ (α00) as it has been derived for α-NiNSal (see part I). In contrast to α-NiNSal the superspace group P^{Ibam}_{11s} (α00) with the additional extinction rule for $(^{m}_{s})$ *hk*0*m*: $m = 2n + 1$ is not an alternative possibility for α-CuNSal because of the existing weak first-order satellites for $l = 0$.

The computer program used for the refinements is described in part I. The function minimized in the full-matrix least-squares refinements was $\sum w(|F_o| - |F_c|)^2$, with weights $w = 1/\sigma^2(F_o)$. The atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The calculations were performed on a Cyber 170 computer.

The positional parameters of the average structure were used as a starting set for the basic structure. In order to fix the origin of the modulation functions the phase term of the Cu^{II} ion was fixed at zero. To avoid oscillation around the *R*-factor minimum a damping factor of 0·5 was applied to the calculated shifts and fast convergence was obtained. All non-hydrogen atoms were refined anisotropically; the positional parameters, amplitudes, phases and phason factors of the H atoms were tied to the corresponding C atoms performing the same shifts. The refinements of the different models were performed only with the reflexions with $I > 2\sigma$ in order to save computing time. The refinement of the best model was then repeated using all observed reflexions ($I > 0$). The large percentage of weak reflexions (65% with $I < 2\sigma$) results in a rather high unweighted *R* factor and deteriorates the weighted *R* factor. This is especially true for the second-order satellites which are generally rather weak. A detailed list of *R* factors obtained at different stages of the refinements is given in Table 1.*

With respect to the results of the refinement of the modulated structure of α-NiNSal (see part I) we have chosen the function $\mathbf{u}_k = \mathbf{A}_k \cos(\mathbf{q}.\mathbf{r}_k + \Phi_k)$ as an harmonic approximation for the actual modulation function. In this case, the displacement vector always lies in a plane. This plane coincides for α-NiNSal with the *ac* plane because displacements parallel to the **b** direction do not exist. Owing to the existence of weak satellites for the layer $l = 0$, indicating displacements parallel to **a** and/or **b**, the plane of the modulation wave of α-CuNSal can be inclined slightly. Anharmonicities have been taken into account for the main displacements parallel to **c** only.

The first refinement, performed with free positional and thermal parameters and individual amplitudes A_z (*i.e.* displacements in the **c** direction), yielded the overall *R* factor $R_w = 0{\cdot}112$ and for the satellites $R_w = 0{\cdot}167$. The introduction of individual phase terms Φ_k for all independent atoms lowered the *R* factors to $R_w = 0{\cdot}071$ and 0·092, respectively.

A refinement with the anharmonic structure factor formula (Table 1*a* of part I) did not further decrease the *R* factors. Therefore we can assume that the modulation functions are merely sinusoidal.

A further significant decrease of the *R* factors, both for the overall and the second-order satellite *R* factor, was obtained including individual phason factors w_k in the structure refinements (for the structure factor formula see Table 1*c* of part I). $R_w = 0{\cdot}065$ (overall) and $R_w = 0{\cdot}084$ (satellites) were obtained.

At the next stage the components of the amplitude parallel to **a** and **b** were included in the refinements. These components were set to zero for the Cu^{II} ion because of its special site symmetry $(^{2}_{1})$. The modulation function, plotted by vectors as a function of *x*, has to obey site symmetry 2 and for our modulation function this condition can only be fulfilled by setting $A_x = A_y = 0$. The *R* factors decreased to $R_w = 0{\cdot}063$ and 0·081, respectively. With this refinement also the weak satellites in the layer $l = 0$, which have very small weights and therefore can be seen as indicators for the quality of the refinement, can be described.

The results of the final refinement with the entire data set (8338 reflexions and 155 parameters) are: for the overall *R* factor: $R = 0{\cdot}176$ and $R_w = 0{\cdot}065$; for main reflexions: $R = 0{\cdot}088$ and $R_w = 0{\cdot}050$; for all satellites: $R = 0{\cdot}265$ and $R_w = 0{\cdot}085$; for satellites with $m = +1$: $R = 0{\cdot}164$ and $R_w = 0{\cdot}078$; $m = -1$: $R = 0{\cdot}184$ and $R_w = 0{\cdot}075$; $m = +2$: $R = 0{\cdot}519$ and $R_w = 0{\cdot}320$; $m =$

* Table 1, the parameters for the H atoms and lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38710 (56 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

-2: $R = 0{\cdot}536$ and $R_w = 0{\cdot}223$. The R factors for the main reflexions are lower than for the refinement of the average structure ($R = 0{\cdot}101$ and $R_w = 0{\cdot}053$). In this refinement an extinction correction was not applied because the extinction factor tended to become negative.

Results and discussion

The final atomic parameters are listed in Table 2. The equilibrium positional parameters are quite similar to those of the average structure (see part II) in contrast to the components U_{33} of the anisotropic temperature factor which decreased considerably. But still they are up to three times larger than U_{11} or U_{22}. A small contribution to U_{33} may stem from the amplitudon factor because the term $2w_k^A$ (see Table 1*c* of part I) cannot be separated. The individual amplitudes A_z decrease from the central atoms to the peripheral atoms, *e.g.* from 4·5% of **c** (0·30 Å) at Cu^{II} to 3·43% (0·23 Å) at C(4). Conversely the phase differences between the Cu^{II} ion and the ligand atoms increase with increasing distance. The phase difference for the N atom is 0·004**a** and for the C(4) atom 0·136**a** (this corresponds to 0·4 and 14·5°, respectively). These results can be interpreted identically to α-NiNSal (see part I), *i.e.* the modulation waves shift the rigid molecule only parallel to the *ab* plane. The amplitudes of the peripheral atoms are damped by steric interactions with the adjacent molecule stacks. The components A_x and A_y are unimportant.

The values of the phason factors w_k^- indicate the same behavior as the amplitudes. The peripheral C atoms have very small values, whereas, for example, for the Cu^{II} ion $w_k^- = 0{\cdot}029$ Å^2 and for the C(8) atom $w_k^- = 0{\cdot}037$ Å^2, where $w_k^- = \langle u_\psi^2 \rangle - \langle u_A^2 \rangle$, *i.e.* the difference between the mean-square atomic displacements which are caused by the fluctuations in phase and those in amplitude. It is generally assumed that the second term is small far away from the phase-transition temperature. In order to explain the decrease of the phason factor for the peripheral C atoms we must assume that the persistent steric interactions between the contact points H(C4)···H(C4^I) of two molecule stacks (see Fig. 2 of part II) do not allow large fluctuations of the phase or amplitude of the modulation wave. The modulation waves of these atoms have to be in phase as far as possible.

Fig. 1 shows the influence of the phason factor on the structure factors for the main reflexions and first- and second-order satellites. The most significant effects can be expected for the main reflexions in the layers with $6 \le l \le 8$ and for the second-order satellites with $l \le 3$. The R factors for these rather weak reflexions, which have only small weights in the refinements, are therefore an appropriate indicator for the physical

Table 2. *Fractional atomic coordinates* ($\times 10^4$), *anisotropic temperature factors* ($\times 10^4$ Å^2), *amplitudes* (*in fractions of* **a**, **b**, **c**, $\times 10^4$), *phases* (*in fractions of* **a**, $\times 10^3$) *and phason factors* $w_k^- = \langle u_\Phi^2 \rangle - \langle u_A^2 \rangle$ ($\times 10^3$ Å^2)

The anisotropic temperature factor has the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	A_x	A_y	A_z	Φ	w_k^-
Cu	0	0	0	418 (1)	445 (3)	785 (2)	0	0	−1 (1)	0	0	450 (1)	0	29 (1)
N	−1263 (1)	667 (1)	−29 (6)	405 (4)	538 (13)	818 (7)	−111 (19)	−52 (17)	57 (7)	76 (4)	−11 (3)	446 (2)	122 (3)	18 (4)
O	1702 (1)	422 (1)	54 (5)	472 (4)	383 (10)	1241 (8)	−148 (20)	−3 (17)	−18 (6)	−23 (5)	−2 (3)	472 (2)	−161 (2)	35 (4)
C(1)	1857 (1)	944 (1)	−99 (5)	532 (6)	614 (17)	818 (10)	144 (23)	227 (15)	22 (9)	−6 (6)	32 (4)	443 (3)	−164 (4)	15 (5)
C(2)	3283 (1)	1171 (1)	−74 (5)	580 (7)	473 (19)	1385 (13)	242 (33)	−106 (25)	−121 (10)	17 (7)	18 (4)	425 (3)	−296 (4)	15 (7)
C(3)	3523 (2)	1707 (1)	39 (8)	678 (7)	706 (20)	1551 (15)	−204 (30)	−187 (27)	−205 (12)	−13 (8)	−7 (4)	400 (4)	−245 (5)	−5 (8)
C(4)	2384 (1)	2091 (1)	−65 (7)	928 (9)	449 (19)	1364 (12)	−58 (32)	−280 (24)	−193 (11)	18 (8)	1 (5)	343 (3)	−102 (6)	0 (1)
C(5)	991 (2)	1881 (1)	34 (8)	742 (8)	483 (19)	1026 (11)	135 (26)	66 (24)	30 (11)	49 (6)	−1 (4)	352 (3)	−35 (4)	17 (5)
C(6)	711 (1)	1324 (1)	−1 (4)	565 (7)	457 (15)	602 (9)	47 (32)	−97 (19)	−27 (9)	−77 (5)	24 (4)	436 (3)	−47 (3)	19 (4)
C(7)	−794 (1)	1142 (1)	−41 (4)	549 (7)	510 (17)	786 (9)	12 (37)	125 (23)	26 (9)	−6 (6)	−1 (4)	402 (3)	77 (4)	15 (5)
C(8)	−2863 (1)	608 (1)	11 (6)	450 (6)	557 (19)	1222 (12)	159 (25)	−355 (14)	57 (9)	41 (4)	−4 (4)	458 (3)	234 (4)	37 (6)

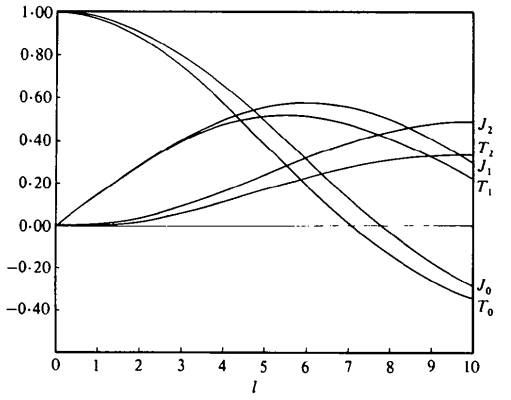

Fig. 1. The plot shows the influence of the phason factor upon the structure factor dependent on the reflexion index l. The functions $T_m(2\pi l.A_z, w_k^-)$ are calculated for the overall amplitude $A_z = 0{\cdot}05$ and for the overall phason factor $w_k^- = 0{\cdot}03$ Å^2. For $w_k^- = 0$ we get $T_m(2\pi l.A_z, 0) = J_m(2\pi l.A_z)$, the Bessel function of order m. The structure factor $F(hklm) = F(hkl) \times T_m(2\pi l.A_z, w_k^-)$.

significance of the R-factor improvements and confirm the model including a phason factor. For example, $R = 0{\cdot}487$ for 37 main reflexions $[I > 2\sigma(I)]$ of the layer $l = 6$ calculated without phason factors and $R = 0{\cdot}320$ for the refinement including phason factors. In comparison, the R factor of the same reflexions calculated from the refinement of the average structure is $R = 0{\cdot}501$. The corresponding R factors for the 58 second-order satellites $[I > 2\sigma(I)]$ of the layer $l = 2$ are $R = 0{\cdot}426$ and $R = 0{\cdot}314$, respectively. The main improvement in the description of the observed structure factors of these sensitive layers is therefore obtained by considering phase fluctuations. The generally high R factors can be explained by the fact that the peaked diffuse background under these weak Bragg reflexions cannot be separated very precisely by fitting the reflexion profiles with two Gaussian curves.

Conclusion

In this report the refinement of the displacively modulated structure of α-CuNSal was discussed under special consideration of the influence of phasons and amplitudons. In contrast to the results of the corresponding Ni phase (see part I) we have now obtained a significantly better description of the observed structure factors when including phason factors in our refinements. A possible explanation could be the higher temperature of investigation (270 K compared to 160 K for α-NiNSal) and therewith the existence of significant thermal effects like phasons and amplitudons. These results and the interpretation of the diffuse scattering (Adlhart *et al.*, 1982) are a reliable indication for the existence of fluctuations of phase and amplitude in the incommensurate phase of α-CuNSal.

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References

ADLHART, W., BLANK, H. & JAGODZINSKI, H. (1982). *Acta Cryst.* A**38**, 505–510.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

STEURER, W. & ADLHART, W. (1983*a*). *Acta Cryst.* B**39**, 349–355.

STEURER, W. & ADLHART, W. (1983*b*). *Acta Cryst.* B**39**, 718–721.

WOLFF, P. M. DE, JANSSEN, T. & JANNER, A. (1981). *Acta Cryst.* A**37**, 625–636.

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X-ray Study of Single Domains of 1,2-Dipalmitoyl-*sn*-phosphatidylcholine with less than 5% Water

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Abstract

Single domains of 1,2-dipalmitoyl-*sn*-phosphatidylcholine dihydrate ($C_{40}H_{80}NO_8P.2H_2O$) have been studied by X-ray scattering experiments. Some new information, which was not accessible by previous observations on powder samples, on the polymorphism of this compound is reported. A quantitative result concerning the molecular packing of the polar heads in the $L\delta$ phase has been deduced from the

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