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## The Structure of the Incommensurate Modulated Phase of $\alpha$ -Bis-(*N*-methylsalicylaldiminato)nickel(II)\*

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### Abstract

The modulated structure of the title compound ( $\alpha$ -NiNSal) was determined at 160 K by single-crystal X-ray methods. The refinements were performed in the superspace group  $P'_{111}{}^{ba2}(\alpha 00)$ . Different models considering thermal fluctuations in the phase and the amplitude of the static modulation wave were calculated. The best refinement yielded the overall  $R$  factors  $R = 0.088$ ,  $R_w = 0.051$  for 4322 independent reflexions including 2725 first-order and 118 second-order reflexions. The positional parameters of the basic structure and of the average structure are nearly equal. The amplitudes of the one-dimensional displacive modulation waves decrease due to steric interactions between adjacent molecule stacks from 0.30 Å at the central Ni<sup>II</sup> ion to 0.22 Å at the peripheral C atoms. The modulation functions were found to be sinusoidal. Calculations with a phason factor yielded only slightly better  $R$  factors – no reliable proof for the existence of amplitude and phase fluctuations.

### Introduction

Incommensurate modulated structures undergo a periodical displacement of the atoms from the positions of the basic structure and/or are modulated in the occupation probabilities or magnetic moments of the atoms. The period of this modulation is incommensurate relative to the period of the basic structure. Until now only a few modulated structures were determined and most of the investigations were dealing with both

displacive and occupation probability modulation, for example Toman & Frueh (1976*a,b*), Kitamura & Morimoto (1977), Böhm (1978), Horst, Tagai, Korekawa & Jagodzinski (1981), Yamamoto & Nakazawa (1982) and Yamamoto (1982). Very few refinements were carried out on mere displacively modulated structures as for example on  $\gamma$ -Na<sub>2</sub>CO<sub>3</sub> (van Aalst, den Hollander, Peterse & de Wolff, 1976). But just these structures and the phase transitions commensurate – incommensurate mostly associated with them are of special interest owing to new lattice dynamical properites (see Axe, 1976, for a review). It is expected that, in addition to the normal modes, there exist phasons and amplitudons corresponding to fluctuations of phase and amplitude of the modulation wave (Overhauser, 1971; Axe, 1980). More recent investigations on biphenyl (Cailleau, Moussa, Zeyen & Bouillot, 1980) show the existence of a phason branch. Theoretical studies of Moncton, Axe & di Salvo (1977) revealed that the ground state of an incommensurate structure does not consist of a mere sinusoidal distortion. Anharmonic interactions always cause additional distortions, being higher harmonics of the primary modulation. The difficulty of proving the existence of smaller anharmonic contributions without a refinement of the modulated structure is because the diffraction harmonics of the primary modulation and the scattering contributions of the higher harmonics coincide. Additional complications result from the influence of the phase and amplitude fluctuations of the static distortion wave.

The intention of the present work was to provide further information about the influence of phasons, amplitudons and higher harmonics besides the determination of the individual modulation functions.

\* IUPAC name:  $\alpha$ -bis(*N*-methylsalicylideneiminato)nickel(II).

## Experimental

The preparation of the crystals, the modus of data collecting at 160 K and the data reduction were described in the preceding paper (Steurer & Adlhart, 1983a) which will be referred to as part I throughout this paper.

9845 reflexions out of 11 227 measured main, first- and second-order satellite reflexions had intensities greater than zero and were classified as observed for the further refinements. The merging of the two data sets collected with different crystal mounting was carried out with the batch scale factors calculated in part I. Considering anomalous-dispersion effects the structure-factor equations (for the structure-factor formulae of Table 1)  $|F(hklm)| = |F(h\bar{k}lm)| = |F(h\bar{k}l\bar{m})| = |F(\bar{h}klm)|$  and  $|F(hk\bar{l}m)| = |F(h\bar{k}l\bar{m})| = |F(\bar{h}kl\bar{m})| = |F(\bar{h}k\bar{l}m)|$ , respectively, are valid. After averaging, 4322 reflexions remained.

Table 1. Structure-factor formulae used in the refinements

The formula (a) is derived in the Appendix, (b) and (c) are taken from Adlhart (1982).  $|\mathbf{Q} = \mathbf{G} - m\mathbf{q}$ ,  $\mathbf{G} = 2\pi\mathbf{H}.f_k(\mathbf{Q})$  is the atomic scattering factor for atom  $k$ ,  $w_k$  the temperature factor,  $\Phi_k$  the phase term,  $\mathbf{A}_k$  the amplitude,  $J_m$  a Bessel function,  $J_m$  a modified Bessel function,  $\langle u_k^2 \rangle$ ,  $\langle u_\psi^2 \rangle$  are mean-square atomic displacements due to fluctuations in the amplitude and phase of the modulation wave,  $\langle \Psi^2 \rangle$  are mean-square phase fluctuations.]

(a) Structure-factor formula including anharmonic contributions

$$F(hklm) = \sum_k \sum_n f_k(\mathbf{Q}) \exp[-w_k(\mathbf{Q})] \\ \times \exp\{2\pi i[\mathbf{H}.\mathbf{r}_k + (m-2n)\Phi_k^1 + n\Phi_k^2]\} J_{m-2n}(\mathbf{Q}.\mathbf{A}_k^1) J_n(\mathbf{Q}.\mathbf{A}_k^2)$$

valid for the superposition of the two functions

$$\mathbf{u}_k^1 = \mathbf{A}_k^1 \sin(\mathbf{q}.\mathbf{r}_k + \Phi_k^1) \text{ and } \mathbf{u}_k^2 = \mathbf{A}_k^2 \sin(2\mathbf{q}.\mathbf{r}_k + \Phi_k^2).$$

(b) Structure-factor formula including the phason factor according to Overhauser (1971)

$$F(hklm) = \sum_k f_k(\mathbf{Q}) \exp[-w_k(\mathbf{Q})] \exp[2\pi i(\mathbf{H}.\mathbf{r}_k + m\Phi_k)] T_m \\ T_m = J_m(\mathbf{Q}.\mathbf{A}_k) \exp(-\frac{1}{2}m^2 \langle \Psi^2 \rangle)$$

valid for the modulation function  $\mathbf{u}_k = \mathbf{A}_k \cos(\mathbf{q}.\mathbf{r}_k + \Phi_k)$ .

(c) Structure-factor formula including the phason factor according to Axe (1980)

$$F(hklm) = \sum_k f_k(\mathbf{Q}) \exp[-w_k(\mathbf{Q})] \exp[2\pi i(\mathbf{H}.\mathbf{r}_k + m\Phi_k)] T_m \\ T_m = \exp(-2w_k^a) \sum_x (-1)^x \exp(-w_k^-) I_x(w_k^-) J_{m-2x}(\mathbf{Q}.\mathbf{A})$$

$w_k^a = \pi^2 l^2 c^{*2} \langle u_k^2 \rangle$  is the amplitudon factor

$$w_k^- = w_k^a - w_k^p$$

$w_k^p = \pi^2 l^2 c^{*2} \langle u_\psi^2 \rangle$  is the phason factor

valid for the same modulation function as (b).

## Structure refinement

The incommensurate phase shows sharp satellites of first and second order besides the main reflexions (Fig. 1). The scattering vector can be written in the form  $\mathbf{Q} = \mathbf{G} - m\mathbf{q}$ ,  $\mathbf{G} = 2\pi(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)$  with  $h, k, l, m$  integers. The satellite vector  $\mathbf{q} = \alpha\mathbf{a}^*$  gives the direction the wave is propagating and the wavelength  $\lambda = a/\alpha$ .  $\alpha$  is an irrational number and a function of temperature ( $\alpha \approx 0.3$  at 160 K).

The intensities of the satellite reflexions and therefore the amplitudes of the modulation functions show a strong temperature dependence (Fig. 2). Satellites cannot be observed in the layer  $l = 0$ . This means that there are only displacements parallel to  $\mathbf{c}$  because the Bessel functions  $J_{m \neq 0}(\mathbf{Q}.\mathbf{A})$  are zero for  $(\mathbf{Q}.\mathbf{A}) = 0$  as is the structure factor for the satellites.

Besides the Bragg reflexions strong diffuse streaks parallel to  $\mathbf{a}^*$  can be seen on Fig. 1. The intensity of these streaks is temperature dependent. Peaks of the diffuse scattering under the main and the satellite reflexions can be observed if two Gaussian lines are fitted to the measured intensity profile. We assume that this diffuse background is caused by phasons as reported for  $\alpha$ -CuNSal (Adlhart, Blank & Jagodzinski, 1982). No diffuse scattering could be found in the layer

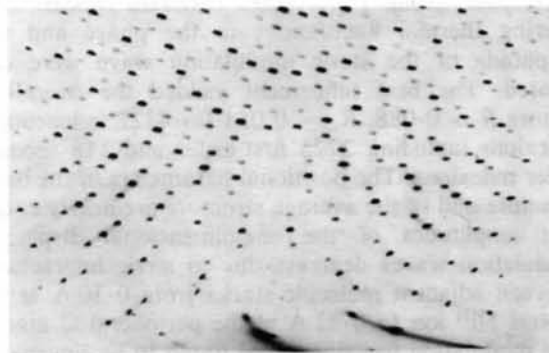


Fig. 1. Section of an  $hk2$  normal-beam Weissenberg photograph at  $T = 190$  K.

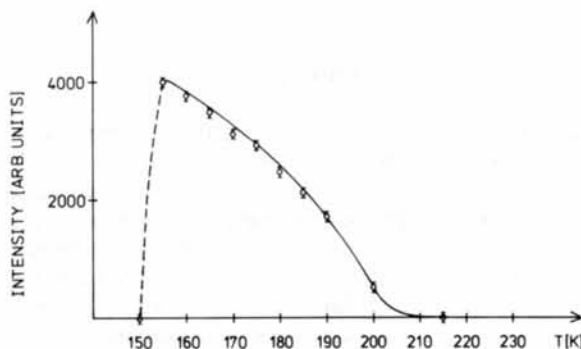


Fig. 2. Intensity of the 1-3, 1, 2 satellite reflexion as a function of temperature.

$l = 0$  so that these dynamical displacements too have components parallel to  $\mathbf{c}$  only.

### (3 + 1)-Dimensional symmetry

From the extinction rules  $hklm: h + k + l = 2n + 1$ ,  $h0lm: h = 2n + 1$  and  $0kl0: k = 2n + 1$ , centering  $I$  and the symmetry elements ( $\frac{q}{2}$ ) and ( $\frac{q}{4}$ ) can be derived according to the (3 + 1)-dimensional superspace-group approach of de Wolff, Janssen & Janner (1982). Therefore, we have the Bravais class  $P_{111}^{lmmm}$  and the possible space groups  $P_{111}^{lba2}$  and  $P_{111}^{lbam}$  ( $\alpha 00$ ), respectively. The non-standard setting  $\alpha 00$  (this means  $\mathbf{q} = \alpha \mathbf{a}^* + 0\mathbf{b}^* + 0\mathbf{c}^*$ ) was chosen to facilitate the comparison with the other phases of  $\alpha$ -NiNSal.

The space groups are generated by the centering [ $I: (x, y, z, t) \rightarrow (1/2 + x, 1/2 + y, 1/2 + z, t)$ ] and the symmetry operations [ $m_x: (x, y, z, t) \rightarrow (1/2 - x, 1/2 + y, z, t)$ ], [ $m_y: (x, y, z, t) \rightarrow (1/2 + x, 1/2 - y, z, t)$ ], [ $2_z: (x, y, z, t) \rightarrow (\bar{x}, \bar{y}, z, \bar{t})$ ] or [ $m_z: (x, y, z, t) \rightarrow (x, y, \bar{z}, t + 1/2)$ ]. A general point in the superspace is thereby denoted as  $(x, y, z, t)$ . The atoms related by  $I$ , ( $\frac{m}{s}$ ) and ( $\frac{q}{4}$ ), respectively, have the same modulation functions (the same phases and mean amplitudes but different actual amplitudes). The symmetry operations ( $\frac{q}{2}$ ) and ( $\frac{q}{4}$ ) invert the satellite vector ( $\mathbf{q} \rightarrow -\mathbf{q}$ ). Consequently, the signs of the phases are changed (the modulation wave is reflected).

### Program for structure refinement

A computer program for refining displacively modulated structures was written on the basis of the Structure Determination Package (SDP) of Enraf-Nonius (Frenz, 1978). The structure-factor formulae shown in Table 1 were programmed. Five new parameters, three for the amplitude vector, one for the phason factor and one for the phase, were added to the normal parameters of each atom. In the case of the anharmonic structure factor the five additional parameters were: two for the amplitudes, two for the phases of the first and second harmonic and one for the phason factor. Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The function minimized in the full-matrix least-squares refinements was  $\sum w(|F_o| - |F_c|)^2$ , the  $R$  factors were defined as  $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$  and  $R_w = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}}{\sum w|F_o|}$  with weights  $w = 1/\sigma^2(F_o)$ . The calculations were performed on a Cyber 170.

The positional parameters of the average structure (see part I) were used as a starting set for the basic structure. The average structure, calculated from the main reflexions only, corresponds to a projection of the  $R_4$  down  $\mathbf{c}$  into the  $R_3$  (de Wolff, 1974). The basic structure is that of the atoms at their equilibrium

Table 2.  $R$  factors obtained from the structure refinements using different models (4322 reflexions)

Positional and thermal parameters were varied in each refinement. The  $R$  factors given in the first column are calculated from all reflexions, in the second from the main reflexions, in the third from the satellites and in the following columns from the satellites with  $m = 1$ ,  $m = -1$ ,  $m = 2$  and  $m = -2$ .

(a) Individual amplitudes, 139 free parameters							
$R$	0.1196	0.061	0.195	0.192	0.195	0.208	0.314
$R_w$	0.0793	0.037	0.177	0.186	0.164	0.226	0.248
(b) Individual amplitudes and phases, 149 free parameters							
$R$	0.0885	0.058	0.128	0.128	0.123	0.159	0.244
$R_w$	0.0512	0.036	0.096	0.116	0.067	0.139	0.147
(c) Anharmonic modulation functions, 170 free parameters							
$R$	0.0886	0.058	0.129	0.127	0.124	0.160	0.257
$R_w$	0.0511	0.036	0.096	0.114	0.068	0.145	0.153
(d) Overall phason factor according to Overhauser (1971), 150 free parameters							
$R$	0.0877	0.056	0.128	0.127	0.122	0.219	0.275
$R_w$	0.0505	0.036	0.095	0.114	0.063	0.214	0.197
(e) Overall phason factor according to Axe (1980), 150 free parameters							
$R$	0.0881	0.057	0.129	0.127	0.123	0.212	0.271
$R_w$	0.0507	0.036	0.095	0.114	0.064	0.206	0.189
(f) Like (e) but refined in the superspace group $P_{111}^{lbam}$ ( $\alpha 00$ ), 115 free parameters							
$R$	0.0870	0.056	0.128	0.126	0.121	0.210	0.268
$R_w$	0.0512	0.037	0.095	0.114	0.064	0.204	0.187

positions (Janner & Janssen, 1977). In order to fix the origin the phase term of the  $\text{Ni}^{II}$  ion was fixed to zero. Owing to the incommensurability a uniform phase shift of the modulation waves and therefore an arbitrary choice of the origin is possible without any energy consumption. To avoid oscillation around the  $R$ -factor minimum a damping factor of 0.5 was applied to the shifts and fast convergence was obtained. All non-hydrogen atoms were refined anisotropically.

At the first stage a refinement was performed with free positional and thermal parameters and individual amplitudes. The hydrogen atoms were set to the same amplitudes as the corresponding carbon atoms. The overall  $R$  factor  $R_w = 0.079$  and the satellite  $R$  factor  $R_w = 0.177$  were obtained (for detailed  $R$  factors see Table 2).

The very different structure factors for some of the satellites with  $m = \pm|m|$  and the satellites around the systematically absent main reflexions ( $0kl: k = 2n + 1$ ) could not be satisfactorily calculated before the introduction of individual phase terms for each non-hydrogen atom. Then the  $R$  factors decreased to  $R_w = 0.051$  (overall) and  $R_w = 0.096$  (for the satellites) (see Table 2).

### Anharmonicities

The second-order satellites may represent so-called diffraction harmonics caused by a perfect sinusoidal modulation wave at  $\mathbf{Q} = \mathbf{G} \pm 2\mathbf{q}_0$  or they may stem from the first anharmonic contribution of the modulation wave with the wave vector  $\mathbf{q}_1 = 2\mathbf{q}_0$ . No

higher-order satellites could be observed, therefore we assumed that possible anharmonicities could satisfactorily be described by the second harmonic. The way to calculate the anharmonic structure factor starting from the modulation functions (atom  $k$ , cell  $l$ , phase  $\Phi_k$ )  $u_k^0 = A_k^0 \sin(\mathbf{q}_0 \cdot \mathbf{r}_{kl} + \Phi_k^0)$  and  $u_k^1 = A_k^1 \sin(2\mathbf{q}_0 \cdot \mathbf{r}_{kl} + \Phi_k^1)$  is shown in the Appendix.\*

The structure refinements were performed with individual amplitudes and phases for the two superposed modulation functions for each non-hydrogen atom. The phase of the second harmonic for Ni<sup>II</sup>, sited on a special position, was fixed to 0.4167 (=  $\lambda/4$ ) in order to obtain mirror symmetry for the anharmonic modulation wave.

The  $R$  factors obtained from these refinements were not significantly lower than for the refinements with harmonic modulation functions (see Table 2). Consequently, the anharmonicities must be small, and further refinements can be carried out with purely sinusoidal modulation functions.

#### *Phason factor according to Overhauser (1971)*

Overhauser found that thermal fluctuations in the phase of the modulation wave could be described by a  $(\mathbf{Q}, \mathbf{A})$ -independent Debye–Waller factor of the form  $T_m = \exp(-\frac{1}{2}m^2 \langle \Psi^2 \rangle)$ . This factor does not have any influence on the main reflexions ( $m = 0$ ) but diminishes higher-order satellites strongly. The argument of the Bessel function  $(\mathbf{Q}, \mathbf{A})$  [see structure factor (b), Table 1] does not refer any more to the mean amplitude of the modulation wave but rather to a fictitious amplitude, which the modulation wave would assume in the absence of fluctuations (Axe, 1980). As a result the amplitudes calculated with that phason factor were increased by about 6 to 10%. Using an overall phason factor, the refinements yielded the  $R$  factors  $R_w^+ = 0.051$  (overall) and  $R_w = 0.095$  (for the satellites) (see Table 2). These  $R$  values are significantly lower than for a refinement without phason factors. [Hamilton (1965) test:  $R_w/R_w^+ = 1.014$ ,  $\mathcal{R}_{1.4172, 0.005} = 1.001$ .] Individual phason factors for each atom did not yield a significant improvement of the  $R$  factors. The second-order satellites were calculated too small generally.

#### *Phason and amplitudon factor according to Axe (1980)*

In contrast to the Debye–Waller factor according to Overhauser (1971), which can be interpreted as a Gaussian phase approximation (GPA), is this one which is  $(\mathbf{Q}, \mathbf{A})$  dependent, not equal to zero for the main reflexions and refers to the mean amplitudes of

the modulation functions. GPA means that the thermal fluctuations of the phase of the modulation wave are assumed to have a Gaussian distribution. Axe derived a Debye–Waller factor for incommensurate modulated structures using the Gaussian displacement approximation (GDA). Thereby the relevant thermal fluctuations are assumed to act in such a way that the atomic displacements have a Gaussian distribution.

The refinements with the structure-factor formula using GDA [formula (c) of Table 1] yielded the  $R$  factors  $R_w^+ = 0.051$  (overall) and  $R_w = 0.095$  (for the satellites). These  $R$  factors are significantly lower than for a refinement without a phason factor [Hamilton (1965) test:  $R_w/R_w^+ = 1.010$ ,  $\mathcal{R}_{1.4172, 0.005} = 1.001$ ]. The final  $R$  values for the refinements using the GPA and GDA, respectively, are quite similar (see Table 2). This fact confirms the finding of Axe (1980) that the GPA and GDA lead to the same results in the small  $(\mathbf{Q}, \mathbf{A})$  small-fluctuation limit. The refinements were performed with an overall phason factor. Individual phason factors did not lower the  $R$  factor significantly.

What we calculated using the structure-factor formula (c) of Table 1 was  $w_k^-$ , the difference between the phason and the amplitudon factor. The term  $2w_k^+$  (amplitudon factor) cannot be separated from  $U_{33}$  having the same derivatives in the structure refinements. This may be one cause for the rather high  $U_{33}$  but it is expected that far away from the second-order phase-transition temperature the phase fluctuations are more important than amplitude fluctuations. A determination of both  $w_k^+$  and  $w_k^-$  would only be possible by studying the diffuse scattering (Adlhart, 1982).

The refinement of the same model in the centrosymmetric superspace group  $P_{115}^{lbam}(\alpha 00)$  yielded significantly higher  $R$  factors (see Table 2).

The further discussion deals with the results of the refinements with the structure factor (c) of Table 1 because, according to the Hamilton test, the  $R$  factor was significantly lower at the  $\alpha = 0.005$  level than for other models without a phason factor. However, one cannot deduce from that alone the existence of phasons and amplitudons considering the very small improvement of the  $R$  factor. Nevertheless it may be interesting to discuss this model with regard to the refinements of the isotypic modulated structure of  $\alpha$ -CuNSal (Steurer & Adlhart, 1983b) in the course of which the introduction of a phason factor decreased the  $R$  factor from  $R_w = 0.071$  to  $R_w = 0.065$ .

## Results and discussion

The refined atomic parameters are listed in Table 3. The positional parameters do not deviate much from the parameters of the average structure (see part I). The thermal parameters behave in the same way except the  $U_{33}$  which were calculated to be much smaller than in

\* The Appendix and the lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38370 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Fractional atomic parameters ( $\times 10^4$ ) with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$A_z$	$\Phi$
Ni	0	0	0	93 (1)	187 (2)	263 (2)	0	0	0 (1)	472 (1)	0
N	-1212 (1)	646 (1)	67 (11)	114 (5)	270 (8)	226 (11)	81 (29)	47 (26)	35 (6)	454 (4)	1036 (53)
O	1701 (1)	406 (1)	22 (11)	107 (4)	173 (6)	478 (11)	-86 (28)	90 (23)	-23 (5)	481 (4)	-1655 (45)
C(1)	1892 (2)	938 (1)	-74 (13)	165 (7)	224 (10)	183 (13)	-26 (37)	-17 (29)	-26 (7)	444 (5)	-1610 (70)
C(2)	3347 (2)	1149 (1)	-24 (16)	168 (7)	257 (11)	405 (15)	17 (49)	-22 (42)	-37 (8)	434 (6)	-2624 (75)
H(C2)	4144 (19)	867 (7)	599 (32)	22 (53)							
C(3)	3615 (2)	1699 (1)	-63 (15)	235 (8)	315 (11)	414 (16)	-101 (40)	65 (35)	-121 (8)	389 (6)	-2217 (85)
H(C3)	4565 (22)	1863 (8)	4 (142)	318 (59)							
C(4)	2475 (2)	2084 (1)	-8 (18)	351 (10)	227 (10)	479 (16)	-45 (61)	-77 (43)	-70 (9)	344 (6)	-909 (105)
H(C4)	2661 (19)	2479 (6)	7 (95)	309 (57)							
C(5)	1058 (2)	1888 (1)	-21 (18)	271 (8)	177 (10)	410 (10)	-17 (43)	-70 (43)	2 (8)	343 (6)	-275 (96)
H(C5)	296 (18)	2156 (7)	199 (67)	169 (56)							
C(6)	752 (2)	1327 (1)	-24 (14)	181 (7)	224 (9)	212 (14)	-49 (46)	37 (35)	-15 (7)	409 (5)	-452 (69)
C(7)	-760 (2)	1148 (1)	-4 (15)	193 (7)	173 (10)	223 (14)	-19 (43)	-24 (42)	30 (7)	419 (5)	672 (68)
H(C7)	-1520 (18)	1453 (6)	167 (66)	142 (47)							
C(8)	-2828 (2)	586 (1)	-32 (15)	115 (6)	243 (8)	402 (15)	-7 (46)	126 (23)	41 (7)	473 (6)	2640 (69)
H(C8)	-3086 (21)	320 (8)	1084 (28)	70 (57)							
H'(C8)	-3094 (29)	464 (9)	-1485 (35)	286 (81)							
H''(C8)	-3297 (20)	934 (7)	405 (48)	281 (64)							

The anisotropic temperature factors have the form  $T = \exp [-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ . The amplitudes  $A_z$  are given in fractions of  $c$  and the phases  $\Phi$  in fractions of  $a$  (one wavelength  $\lambda = 1/q \approx 3.33a$ ). The result for the phason factor is  $\langle u_z^2 \rangle - \langle u_z^2 \rangle = 0.0153 (5) \text{ \AA}^2$ .

the average structure. But now, as before, the  $U_{33}$  are mostly substantially greater than the  $U_{11}$  and  $U_{22}$  respectively. This may be caused to some extent by the contribution of the amplitudon factor  $2w_k^A$  to the normal Debye-Waller factor. The calculated phason factor would correspond to fluctuations in the phase of the modulation waves comparable with the normal Debye-Waller factor. The value of  $\langle u_z^2 \rangle = 0.0153 (5) \text{ \AA}^2$  corresponds to the value of  $\langle \Psi^2 \rangle = 0.181 (4) \text{ rad}^2$  obtained from the calculations with the phason factor according to Overhauser (1971).

The individual amplitudes show a continuous decrease from 4.7% of  $c$  (0.30 \AA) at the central Ni<sup>II</sup> ion down to 3.4% (0.22 \AA) going to the peripheral C(4) atom. Conversely, the phase differences between the Ni<sup>II</sup> ion and the ligand atoms increase with increasing distance. The phase difference for the O atom is 0.0046  $a$  and for the C(4) atom 0.1566  $a$ , for instance. To interpret these results we have first to discuss two opposing models. A rigid molecule constrained in a rigid molecule stack could only perform simultaneous parallel shifts of all atoms (the actual amplitudes of the atoms would be equal). The modulation functions would have phase differences proportional to the  $x$  parameters of the atoms (see Fig. 3*a*). On the other hand, a perfectly flexible molecule would have modulation waves with equal phases and different actual amplitudes (Fig. 3*b*). If we view the crystal structure (see Fig. 5 of part I) we can see that one molecule stack is surrounded by six others which are related by symmetry and, consequently, have the same modulation functions. The Ni<sup>II</sup> ions adjacent along the  $a$  direction have a difference in the  $x$  parameter of 1 and are shifted by the modulation by as much as 0.5 \AA from each other. The Ni<sup>II</sup> ions related by the glide planes have a phase

difference due to the  $x$  parameter of 1/2 and will be shifted as much as 0.25 \AA. If we assume the first model to be valid these shifts would be the shifts of the entire columns and would cause strong steric interactions at the contact points [H(C4)-H(C4)']\* for instance]. Using the second model the shifts of the columns (represented by the Ni<sup>II</sup> ions) would be compensated for by tilting and bending the molecules according to the equally phased modulation waves and there would not exist any steric hindrances at the contact points.

\* The superscript  $i$  refers to the adjacent molecule.

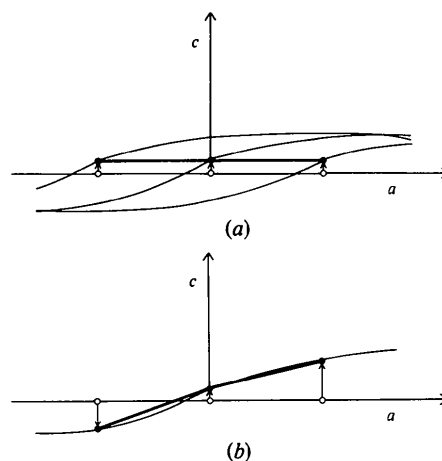


Fig. 3. (a) The modulation functions  $u_k$  have phase shifts proportional to the positional parameter of each atom. The actual amplitudes are equal for all atoms. (b) The modulation functions have the same phases. The actual atomic displacements are different.

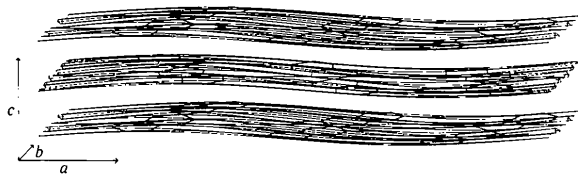


Fig. 4. The modulation waves for three molecule layers ( $z = 0, z = 1/2, z = 1$ ) over one period. The displacements parallel to  $c$  are magnified by a factor of 2.

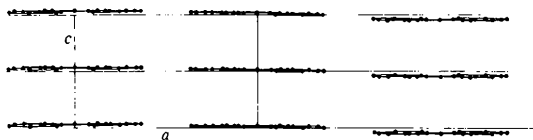


Fig. 5. Projection of three molecule layers down  $b$  to show the parallel shift of the molecule stacks due to the modulation wave over one period.

If we look now at the results of the structure refinement we can interpret them in the way that the ligand atoms around  $Ni^{II}$ , which are close packed between the adjacent molecules at  $z = 1/2$  and  $z = -1/2$ , behave as a rigid body (the phase terms are nearly equal to the  $x$  parameters). The benzene-ring atoms C(2) to C(5), which stand out of the columns and are less rigid, are riding on modulation waves with smaller phase differences minimizing the interactions with the adjacent columns in this way (the phase terms are far from the values of the  $x$  parameters). Since the molecules are too rigid for an optimal phase adjustment the amplitudes of the peripheral ligand atoms are damped additionally.

Fig. 4 shows the modulation functions and Fig. 5 a projection of the modulated structure down  $b$  to illustrate the way the molecules are moved. One can see that the tilt of the molecules is rather small, otherwise the lattice constant  $c$  would have to be increased.

The results of a thermal motion (TLS) analysis (Schomaker & Trueblood, 1968) of the basic structure are presented in Table 4. The calculations were carried out with *XANADU* (Roberts & Sheldrick, 1976). In comparison with the TLS analysis of the average structure (see part I) the translational component parallel to  $c$  has decreased and the librational term around  $b$  became smaller for the entire molecule. The libration tensor for the half molecule remained nearly unaltered. Hence, the basic structure performs the 'fluttering' motion independent of the modulation.

### Conclusion

In this report the refinement of the displacively modulated incommensurate structure was discussed considering the influence of phasons, amplitudons and

Table 4. Thermal motion analysis (TLS) calculated for the basic structure of  $\alpha$ -NiNSal at 160 K

In (a) the entire molecule and in (b) the half molecule were assumed to be rigid bodies. Results for the T, L and S tensors with e.s.d.'s in parentheses are given.  $R_g$  gives the agreement between observed and calculated  $U_{ij}$ , weights were assigned to the atoms according to their atom number.

(a) Entire molecule		
Center which gives symmetric S		
0.0000	0.0000	-0.1160
L (rad <sup>2</sup> )		
0.0008 (2)	0.0003 (2)	0.0000 (1)
	0.0018 (3)	0.0000 (2)
		0.0009 (1)
S (rad Å)		
-0.0004 (1)	0.0002 (4)	0.0000 (2)
	0.0009 (12)	0.0000 (3)
		-0.0005 (11)
T (Å <sup>2</sup> )		
0.0087 (14)	0.0007 (11)	0.0000 (12)
	0.0196 (11)	0.0000 (10)
		0.0201 (16)
$R_g = 0.199$		
(b) Half molecule		
Center which gives symmetric S		
-0.0014	0.0558	-0.0516
L (rad <sup>2</sup> )		
0.0043 (9)	0.0021 (8)	0.0008 (4)
	0.0039 (8)	0.0006 (3)
		0.0009 (2)
S (rad Å)		
-0.0008 (11)	0.0005 (7)	-0.0015 (5)
	0.0014 (11)	0.0000 (6)
		-0.0006 (10)
T (Å <sup>2</sup> )		
0.0106 (12)	0.0007 (10)	0.0027 (13)
	0.0195 (12)	0.0001 (11)
		0.0147 (23)
$R_g = 0.143$		

anharmonicities. The mechanism of the first-order phase transition discussed in part I was confirmed by the results of the structure refinement. The existence of phasons and amplitudons, respectively, could not be reliably shown by the refinements even though the diffuse scattering can be interpreted in this way. Refinements of the modulated structure of the isotopic compound  $\alpha$ -CuNSal, which shows much stronger diffuse scattering, will supply more information on that.

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## 1-Methyl-4-imidazoline-2-thione:\* Structure, Comparison with Related Molecules and a Discussion of Coordination Characteristics

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### Abstract

$C_4H_6N_2S$ ,  $M_r = 114.1$ , triclinic,  $P\bar{1}$ ,  $a = 7.338$  (12),  $b = 7.068$  (1),  $c = 11.589$  (4) Å,  $\alpha = 106.82$  (6),  $\beta = 99.79$  (2),  $\gamma = 93.21$  (5)°,  $U = 563.5$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.35$  (1),  $D_x = 1.35$  Mg m<sup>-3</sup>,  $\mu(Cu K\alpha) = 3.874$  mm<sup>-1</sup>,  $F(000) = 240.0$ ; final  $R = 0.0562$  for 1687 counter reflections. The asymmetric unit consists of two molecules linked *via* N–H...S bonds [N(32)...S(21) = 3.315 (5); N(31)...S(22) = 3.363 (5) Å]. Average distances for the two independent molecules are C(2)–S(2) = 1.685 (2); C(2)–N(1) = 1.351 (4); C(2)–N(3) = 1.345 (3); N(3)–C(4) = 1.387 (4); N(1)–C(5) = 1.374 (3); C(4)–C(5) = 1.333 (5); and N(1)–C(1) = 1.464 (4) Å. These results are compared with those of related molecules. Coordination of mimt produces a

lengthening of the C(2)–S(2) bond as well as ‘twisting’ and ‘tilting’ of the molecule in order to facilitate metal–ligand  $\pi$  interactions.

### Introduction

The imidazolethione system is known to possess wide-ranging pharmacological activity including central nervous system depressant and acticonvulsant properties (Kohn, Kohn, Steenberg & Buckley, 1977), as well as bacteriostatic (Foye & Ho, 1972) and thyrostatic activity (Jemec, 1970). The search for carcinostatic compounds has been extended to the nucleosides (Gosselin, Imbach, Townsend & Panzica, 1979) and metal complexes (Dehand, Jordanov & Beck, 1975) of imidazolethiones.

Prominent among this group of compounds is 1-methyl-4-imidazoline-2-thione (mimt) which is known primarily for its thyrotoxic activity and is commer-

\* Also known as 1-methyl-2(3*H*)-imidazolinethione.

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