

## The Crystal Structure of $\text{Ni}_{6\pm x}\text{Se}_5$

ERLING RØST and KJELL HAUGSTEN

*Kjemisk Institutt A, Universitetet i Oslo,  
Blindern, Oslo 3, Norway*

A high temperature phase with approximate composition  $\text{Ni}_6\text{Se}_5$  has been described by several authors. According to Grønvold, Møllerud and Røst<sup>1</sup> the structure is orthorhombic with the lattice dimensions  $a=3.437$ ,  $b=11.86$ , and  $c=17.06$  Å. Possible space groups are  $Cmcm$ ,  $Ama2$  and  $Cmc2_1$ . The phase is stable between approximately 400 and 640°C.

It is difficult to obtain the pure phase in quantities large enough for density measurements. In the ternary systems Ni-Se-Te<sup>2</sup> and Ni-S-Se,<sup>3</sup> however, density measurements have been carried out on the corresponding phase. In all cases the unit cell was found to contain 20 chalcogene atoms whereas certain variations were observed in the amount of nickel. The results strongly indicate that the stoichiometric composition of the binary phase is  $\text{Ni}_{24\pm x}\text{Se}_{20}$ .

Single crystals were obtained by transport reactions at about 640°C with iodine as transporting agent. The crystals show a tendency of forming superstructures, but the extra reflections are very weak and are disregarded in the present study. A crystal, 0.06 mm long and with a cross section of 0.03 by 0.03 mm, was used in the X-ray investigation. Intensity data were obtained in an integrating Weissenberg camera using  $\text{MoK}\alpha$ -radiation. In the

layers  $0kl-3kl$  360 independent reflections were observed. The intensities were estimated photometrically and visually. Corrections for X-ray absorption were made by assuming the crystal to be cylindrical. No corrections were made for secondary extinction. The structure was determined by three dimensional Patterson and Fourier synthesis, and the parameters were refined by a full matrix least squares programme.<sup>4</sup> Refinements were carried out for each of the space groups mentioned above, but the structure was found to be about the same in all cases.

Since the present determination of the structure only concerns the subcell of a superstructure lattice a detailed discussion of the different symmetries is of only limited interest. Therefore, the results referring to only one space group,  $Cmcm$ , is presented in Table 1. A projection of the structure projected along  $[100]$  is shown in Fig. 1. The reliability factor  $(\sum|F_o| - |F_c|)/\sum|F_o|$  is 0.088. The calculations suggest that the nickel positions Ni6 and Ni7 only can be determined in the superstructure unit cell, and in the present calculations only 50 % occupancy is assumed for these positions. These positions are shown as dotted circles in Fig. 1. This implies a deficit of nickel atoms compared to the assumed stoichiometry. With the present set of intensity data, however, no further acceptable nickel positions could be found. To solve this problem it is necessary to make a detailed investigation of the superstructure.

The interatomic distances are given in Table 2. Those concerning the Ni6 and Ni7 atoms, which cannot be satisfactorily determined in the subcell, are given in

Table 1. Positional parameters ( $x,y,z$ ), temperature factors ( $B$ ), and estimated standard deviations for  $\text{Ni}_{6\pm x}\text{Se}_5$ .<sup>a</sup>

	$x$	$y$	$z$	$B$
Se1 in 4(c)	0	.1393(4)	.25	.34
Se2 in 8(f)	0	.1171(3)	.6515(2)	.78
Se3 in 8(f)	0.5	.1202(3)	.4509(2)	.89
Ni4 in 4(c)	0	.3408(5)	.25	.28
Ni5 in 8(f)	0.5	.0329(4)	.3248(3)	.37
Ni6 in 8(f)	0.5	.3137(8)	.4735(6)	.71
Ni7 in 8(f)	0.5	.4853(9)	.0271(7)	1.16

<sup>a</sup> For the positions Ni6 and Ni7 only 50 % occupancy is assumed.

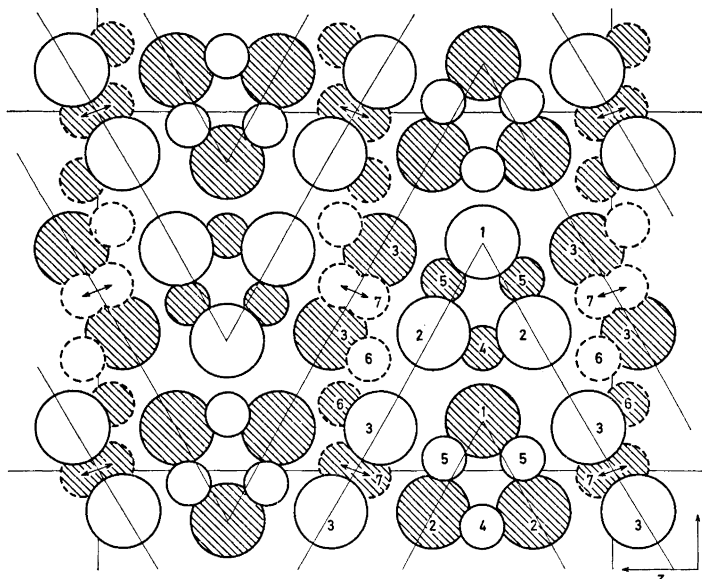


Fig. 1. A projection on [100] of one subcell of  $\text{Ni}_{6\pm x}\text{Se}_5$ . The large circles represent selenium atoms and the small ones nickel atoms. The atoms for which  $x=0$  are shown as hatched circles. Open circles represent atoms at  $x=0.5$ .

Table 2. Interatomic distances (in Å) in  $\text{Ni}_{6\pm x}\text{Se}_5$ . Those concerning the partly occupied positions are given in parenthesis.<sup>a</sup>

Se1—Se2	3.47	Se3—Se3	3.31
—Ni4	2.39	—Ni5	2.39
—Ni5	2.48	—Ni6	(2.33)
Se2—Se2	3.36	—Ni6	(2.29)
—Se5	3.57	—Ni7	(2.38)
—Ni4	2.45	—Ni7	(2.49)
—Ni5	2.51	Ni5—Ni5	2.55
—Ni6	(2.29)	—Ni4	2.61
—Ni7	(2.45)	Ni6—Ni6	(2.46)
		—Ni7	(2.04)
		—Ni7	(2.55)

<sup>a</sup> Along the  $a$ -axis the atoms are repeated at distances of 3.44 Å.

parenthesis in the table. The selenium atoms form a zig-zag pattern in the  $bc$  plane. The nickel atoms in the positions Ni5 and Ni4 are both coordinated by five Se-atoms in pyramidal arrangements with Ni—Se distances in the range 2.39 to 2.51 Å. The Ni6 positions are surrounded

tetrahedrally by selenium atoms at distances 2.29 and 2.33 Å. The rather short distances should be regarded together with the reduced occupancy of position Ni6. The Ni7 atoms are distributed around an octahedral position in the selenium lattice. It seems likely that the superstructure will show an alternating occupancy of the positions Ni7.

In a recent abstract Fleet<sup>5</sup> reports the determination of the structure of  $\text{Ni}_7\text{S}_6$ . Details of the structure are not presented, but there is obviously a similarity between this structure and  $\text{Ni}_{6\pm x}\text{Se}_5$ . However, the unit cell content is given as  $\text{Ni}_{21}\text{S}_{18}$ , and in contrast to the present study reduced occupancy is assumed both for nickel and chalcogene positions.

After this work was finished a crystal with a more pronounced superstructure was obtained. Oscillation and Weissenberg photographs of this crystal show that both the  $a$ - and the  $b$ -axis have to be doubled. A more detailed determination of the structure is planned.

The intensity data from the present investigation can be obtained on request.

1. Grønvoid, F., Møllerud, R. and Røst, E. *Acta Chem. Scand.* **20** (1966) 1997.
2. Røst, E. and Vestersjø, E. *Acta Chem. Scand.* **22** (1968) 2118.
3. Haugsten, K. and Røst, E. *Acta Chem. Scand.* **23** (1969) 3599.
4. Dahl, T., Gram, F., Groth, P., Klewe, B. and Rømming, Chr. *Acta Chem. Scand.* **24** (1970) 2232.
5. Fleet, M. E. *Am. Cryst. Ass., Summer meeting 1971, Iowa State University, Ames, Iowa, Program and Abstracts*, p. 58.

Received September 27, 1971.

## The Valence Electron Density Distribution of Strained Single Bonds in the Iterative Extended Hückel Approach. VI. The First Excited State Charge Density of Bicyclobutane \*

O. MARTENSSON

*Quantum Chemistry Group, Uppsala University, Box 518, S-751 20 Uppsala 1, Sweden*

The intention of this series of papers and related articles<sup>1,2</sup> has been to investigate to what extent the distribution of the valence charge can give information about the nature of strained single bonds and the interpretation of the valence concept in ground state molecules. Since fairly big molecules are treated, the iterative extended Hückel method was chosen. The results have been presented in the form of density level diagrams of pertinent sections of the molecules. In the case of strained single bonds, two maxima outside the classical valence line were obtained, a result which is in accordance with those obtained by more sophisticated methods

\* Sponsored in part by King Gustaf VI Adolf's Fund for Swedish Culture, Knut and Alice Wallenberg's Foundation and in part by the Swedish Natural Science Research Council.

on small molecules, for instance cyclopropane.<sup>3,4</sup> That this heaping up of charge outside the interatomic, straight line will be more pronounced when two or three cyclopropanes are "fused" together as in bicyclobutane and tricyclobutane, seems obvious. Chemically strained single bonds show some resemblance to the unsaturated bond, but this similarity is not reflected in the valence charge distributions, which are of quite different types in the two cases.

Although the IEH method is fairly naive, it has in calculations of this type the advantage of taking all overlap integrals between the valence orbitals under consideration. Therefore it might be of interest also to look at the first excited state densities. It should also be pointed out that the picture given of the first excited state charge density is a crude one also for the reason that excitation generally leads to deformation of the molecule and that calculations for molecules in excited states have to be based on another geometry than when the ground states are treated. To obtain easily interpreted density difference diagrams for semiquantitative considerations one prefers to have the same geometry.

The bridge bond of bicyclo[1.0.1.]butane was selected as an example of a strained single bond. The ground state charge density of this molecule has been treated by me some years ago,<sup>5</sup> but new structural data obtained from the microwave studies by Cox *et al.*<sup>7</sup> make a recalculation desirable. These data and others<sup>8</sup> indicate a considerably smaller value for the C-C-H bridgehead angle than that by Haller and Srinivasan<sup>9</sup> used by me earlier. These new calculations also incorporate the value of

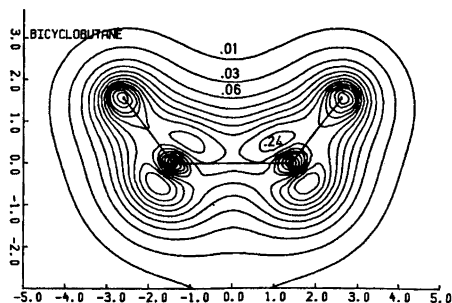


Fig. 1. Valence charge distribution of bicyclobutane in the symmetry plane through the bridgehead line. Ground state.