

08.X-1 ENDOTAXY AND PARACRYSTALLINITY. By A. Preisinger and H. Ludwiczek, Institut für Mineralogie, Kristallographie und Strukturchemie, Techn.Univ. Wien, A-1060 Wien, Austria.

Description of condensed state by statistics: Statistics of distances, statistics of coordinations and statistics of translations. An increase of the concentration of distortions in a lattice leads to a disturbed lattice. One of these disturbed lattices is the paracrystalline lattice described by the statistics of translations in which parallel to one direction the distance of equivalent lattice points on "lattice rows" are statistically independent random variables ("longitudinal correlation" = 0).

Two mathematical-statistical models exist: One with "transversal correlation" = 1 and one with "transversal correlation" < 1. The first one is homogeneous and infinite, the second one is inhomogeneous and of finite size. Only the last model is realized in nature, it is called "paracrystal".

The cause of paracrystallinity is the random distribution of small atomic groups endotactically built into a lattice. The endotaxy of atomic groups leads to relationships of the distortions in different lattice directions ("endotactical correlation"), which can be analyzed by high precision line profile analysis. In the case of the ammonia catalyst the chemical nature, the concentration and the orientation of endotactic groups, and the thermal stability of paracrystals will be given.

08.X-2 ELECTRON MICROSCOPY OF DOMAIN STRUCTURES IN MINERALS. By J. Van Landuyt, University of Antwerp, RUCA, Groenenborgerlaan 171, B-2020 Antwerp, Belgium.

The fragmentation of single crystals in domains often hampers the structure determination of materials and minerals especially if their presence is unexpected or their character unknown. Domain structures often result from a lowering of symmetry upon structural transformation or ordering. The characterisation of the atomic configurations can give us information on the physical processes involved in these transitions.

Electron microscopy and diffraction offers a unique tool for visualizing these domains beyond the high resolution optical microscopy scale and to characterize them crystallographically.

Different types of domain structures will be reviewed and their visibility criteria will be discussed. It will be shown how diffraction contrast and high resolution microscopy, almost invariably complemented by electron diffraction observations can yield very detailed information on domains and the interface between them such as antiphase boundaries, twin domain boundaries, inversion boundaries, etc. It will be shown how observables such as fringe patterns at inclined boundaries, extinction of contrast for certain reflections, background intensity differences, dark field images in relevant reflections etc., contribute to determine displacement vectors of the boundaries, and the relative orientation of the structures at the boundaries between variants. The available high resolution capabilities of electron microscopes now also enable structure projections to be imaged which under certain conditions are directly interpretable in terms of atomic models as well for the perfect as for the domain fragmented structures.

Illustrations will be mainly taken from mineral studies and particular attention will be paid to a particular dauphiné twin domain configuration giving rise to an incommensurate phase near the  $\alpha \rightarrow \beta$  transition in quartz.

08.X-3 ABOUT IMPERFECTIONS IN THE ANION

PACKING OF SULFIDES. By G.B.Bokij, M.T.Dmitrieva and Yu.P.Dikov, Institute for Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry of the USSR Ac. of Sci., Moscow, USSR.

The work is devoted to the further development of the idea about the presence of the hydrosulfide ion  $HS^-$  in sulfides. The idea was suggested earlier by one of the authors and it allows to explain non-stoichiometry, often observed in sulfides, from the positions of crystal chemistry (Bokij, Bondar. Dokl. AN SSSR. (1979) 248, 956). Hägg's classical hypothesis, of 1933, (Hägg, Suchsдорff. Zs. Phys. Chem. (1979) B.22, 444) explaining the non-stoichiometry of pyrrotines by the formation of the metal's vacancies as a result of the partial replacement of the  $Fe^{2+}$  by  $Fe^{3+}$  was not confirmed by Mässbauer's method ( $Fe^{3+}$  was not found in pyrrotines). An explanation of this fact was suggested by Belov. Ocherky po strukturnoy mineralogii. M.: Nedra, 1976, s. 313). But the problem of non-stoichiometry in sulfides has not yet been solved.

In this work sphalerite served the object under investigation, the samples of which were prepared by the hydrothermal synthesis with different concentrations of  $HS^-$  ions (pH in the solution changes from 0 to 14).

The samples were investigated by X-ray and X-ray photoelectronic spectroscopy methods. The elementary cell parameters in the investigated samples are determined with a precision of 0,0005Å and they change from 5.4106<sub>5</sub>Å to

5.4070<sub>5</sub>Å (for different points of the system).

As it was expected, the samples synthesized with the maximum  $HS^-$  ions concentration in the solution have the minimal  $a_0$  values.

In the investigation of the samples by the X-ray photoelectronic spectroscopy method (2p and 2s are sulfur lines and 2p, 3s, 3p and 3d are zinc lines) special attention was paid to sulfur lines, which have a constant and well-reproduced low-energy shoulder at the distance of 1,3-1,5 eV from the main maximum. The bound energy, corresponding to this shoulder, appears to be the closest to the electron bound values of the  $S^{2-}$ , which is a part of the  $HS^-$  group. The maximum intensity of this shoulder corresponds to the ZnS sample with a minimal  $a_0$  value. It is logically to explain the results obtained by the presence of  $HS^-$  groups in the ZnS structure, that leads to the decrease of the  $a_0$  parameter. Laying no claim to the whole replacement of all existing hypotheses, our hypothesis is the first to explain the imperfections in the anion part of the ZnS structure as a result of changing  $S^{2-}$  for  $HS^-$ , which causes vacancies in the cationic part.

<sup>x</sup>Inst. of Cryst. Ac. Sci. USSR