СРПСКО КРИСТАЛОГРАФСКО ДРУШТВО
и
ИНСТИТУТ ЗА НУКЛЕАРНЕ НАУКЕ „ВИНЧА"

SERBIAN CRYSTALLOGRAPHIC SOCIETY
and
VINČA INSTITUTE OF NUCLEAR SCIENCES

III КОНФЕРЕНЦИЈА
СРПСКОГ КРИСТАЛОГРАФСКОГ ДРУШТВА
Изводи радова

III CONFERENCE
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ПРЕДГОВОР

Трећа конференција Српског кристалографског друштва (СКД) одржана је 29. и 30. септембра 1994. год. у Новом Саду под покровитељством Српске академије наука и уметности (САНУ) и уз финансијску помоћ Министарства за науку и технологију Републике Србије (МНТРС).

Трећа Скупштина СКД је одржана 30. 9. 1994. год. у Новом Саду у згради САНУ, са почетком у 18 часова са следећим дневним редом:

1. Отварање Скупштине и Извештај о раду СКД у периоду између две конференције,
2. Финансијски извештај,
3. Будуће активности СКД.

1. Отварање Скупштине и Извештај о раду СКД у периоду између две конференције

Академик Бела Рибар, председник СКД, отворио је Скупштину и поздравио присутне госте и чланове друштва. Обавестио их је да је СКД у периоду између II и III Конференције учлањено у Европски кристалографски комитет (ЕСС). Проф. др С. Станковић присуствовала је као делегат СКД седници ЕСС која је одржана у Дрездену (Немачака). У истом граду од 28. августа до 2. септембра 1994. год. одржан је XV Европски кристалографски састанак у чијем су раду учествовала три члана друштва. У истом периоду прикупљени су, обрађени и послати подаци о свим члановима СКД за IX издање публикације „World Directory of Crystallographers", штампани су Изводи радова I и II Конференције СКД и организована III Конференција. На III Конференцији су одржана три пленарна предавања и 18 научних саопштења. Прво пленарно предавање одржао је гост СКД проф. А. Ка́лма́н из Будимпеште, друго проф. С. Никетић (Хемијски факултет, Београд) и треће др Д. Родић, научни сарадник (Институт за нуклеарне науке „Винча", Београд).

2. Финансијски извештај

Прочитан је и прихваћен финансијски извештај који је поднео секретар СКД. С обзиром на нашу тешку ситуацију постоје проблеми са уплатом годишње чланарине Интернационалној унији за кристалографију (IUCr) за 1994. год. У току 1994. год. од IUCr као нови чланови добијали смо бесплатно часописе Acta Cryst. A, B, C, D и J. Appl. Cryst., а за наредну годину питање претплате још увек није решено. Што се тиче чланарине, она остаје 10, а за студенте 5 динара.

3. Будуће активности СКД

Скупштина се сагласила да се IV Конференција одржи у септембру 1995. год. на Борском језеру или у Новом Саду и да се на Конференцију позову кристалографи из суседних земаља. Размотрана је и могућност организовања заједничке српско-мађарске кристалографске конференције. У складу са Статутом СКД потребно је за следећу годину припремити изборе нових чланова Председништва СКД. Скупштина је предложила да се извиди могућност прикључења неком националном кристалографском центру за добијање датотеке „Cambridge Data File" уз одговарајућу финансијску надокнаду. Усвојено је да се пленарна предавања и изводи III Конференције штампају само на енглеском језику, а по жељи аутора радови могу бити штампани у целини.

Од Југословенског библиографског института ова публикација је добила ознаку ISSN 0354-5741. Она садржи пленарна предавања и изводе или радове у целини који су саопштени на III Конференцији СКД. Сви радови су штампани офсет-техником без накнадних корекција. Свако пленарно предавање је означено ознаком P и редним бројем, а саопштење ознаком S и одговарајућим редним бројем.

У Београду, јануар 1995.   Уредници

PREFACE

The III Conference of the Serbian Crystallographic Society (SCS) was held in Novi Sad on September 29-30, 1994 under the auspices of the Serbian Academy of Sciences and Arts (SASA) and with financial support of the Ministry for Science and Technology of the Republic Serbia (MSTRS).

The Assembly of SCS was held on September 29, 1994 in Novi Sad with the following agenda:

1. Opening ceremony and the report of the activity of the SCS between the two conferences,
2. Financial report,
3. Further activities of SCS.

1. Opening ceremony and the report of the activity of the SCS between the two conferences

The session was opened by prof. Bela Ribar, the member of the SASA and president of the SCS. After welcoming the guests and the members of the SCS, he reported that between the II and III conferences SCS has been accepted as the member of European Crystallographic Committee (ECC). Prof. Dr. S. Stanković as the deputy of SCS with some of the members of SCS attended the 15th European Crystallographic Meeting in Dresden, Germany, Aug. 28 - Sept. 2, 1994. The data for all members of SCS for the IX edition of *"World Directory of Crystallographers"* were prepared. The abstracts *I and II Conference of the Serbian Crystallographic Society* is published. At the III Conference, the three plenary lectures and 18 scientific reports were presented. Prof. Dr. A. Kálmán, the guest of SCS from Budapest, held the first plenary lecture, the second was presented by Prof. Dr. S. Niketić (Faculty of Chemistry in Belgrade) and the third plenary lecture was presented by Dr. D. Rodić, research associate in the Institute for Nuclear Sciences "Vinča" in Belgrade.

2. Financial report

The Financial report of the secretary of SCS was accepted. Because of difficult financial situation, there is a problem with payment of annual subscription to the IUCr for 1994. During the current year as a new member of IUCr we have received Acta Crystallographica A, B, C and D and Journal of Applied Crystallography free of charge. For the next year this problem has to be solved. Annual fee for the members of SCS is 10 and 5 din. for the students.

3. Further activities of SCS

The Assembly of SCS suggested and confirmed Bor Lake or Novi Sad as the locations for the IV Conference of SCS which will be held in September 1995. The invitations should be send to the crystallographers of neighboring countries. The possibility of the mutual Serbian-Hungarian conference was discussed. According to the Statute of SCS it is necessary for the next year to prepare elections for the Presidency of SCS. The Assembly of SCS suggested to explore the possibilities of our cooperation with some national crystallographic centres in order to get an access to Cambridge Data File with corresponding financial payment. It is accepted that the plenary lectures and abstracts of the III Conference will be printed only in English and on the request of authors could be printed in full.

From the Yugoslav Bibliographic Institute this publication has got the sign ISSN 0354-5741. The publication contains the plenary lectures and abstracts or full papers of lectures presented at the III Conference of SCS. The papers are printed by offset technique as submitted by authors. Each plenary lecture is labelled with P and abstracts by S followed by a serial number.

Belgrade, January 1995   Editors

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Similarity and dissimilarity between the crystallographic phenomena: isostructuralism and polymorphism

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The *governing principle* of all kinds of molecular associations is the striving for attainment of the maximum density of material by bringing the bumps of, in general, amorphous molecules into the hollows of the adjacent molecules via the optimum symmetry operations permitted within the seven crystal systems. Even the simplest crystal is the product of infinite translations of identical molecules in three dimensions. This is termed as a *homomolecular* association. Within this large class of associations *homochiral, heterochiral* and *achiral* crystal structures are distinguished.

Strictly speaking we use the term *molecular association* when two or more molecules form a crystal lattice via co-crystallization and the asymmetric unit of the new lattice provides room for at least one molecule of each component. When the properties of the individual components are very largely conserved in these intermediate phases of A_xB_y type, they are called "binary adducts".

Since Mitscherlich's discovery (1819) the isomorphism of crystals has been interpreted in various, sometimes controversial ways. Recently Kálmán and coworkers (1993) recommended the exclusive use of the term *isostructural* for organic crystals. In addition, starting from the "main part" isostructuralism of cardenolides and other steroids and using the results of Bernstein and coworkers (1987) they set up a classification of the *forms* and *degrees* of isostructuralism exhibited by organic molecules. From these analyses it was revealed that, beyond the *highly* isostructural pairs there are *similar crystal structures* which are related only by relaxed packing rules. They are termed as *homeostructural* pairs.

The different forms of *polymorphism* (conformational, electronically induced, irreversible, pseudo, etc.) enable us to understand those molecular properties and interactions which have influence on biological procedures. The differences between the various polymorphs (at least dimorphs) of a compound manifest themselves as differences in solubility, rate of dissolution, and vapour pressure. Such effect can be very important in pharmaceutical applications, e.g. the tableting behaviour of powders, physically stable dosage forms and chemical stability are equally dependent on it. This made X-ray diffraction (single crystal studies and powder diffractograms, as well) indispensable in the scientific evaluation of different polymorphs of drugs.

Heteromolecular (binary) systems along with polymorphism may also exhibit isostructuralism. Recently, Caira and Mohamed (1992) reported three solvates of 5-methoxysulfadiazine formed with (a) dioxane, (b) tetrahydrofuran and (c) chloroform. These three clathrates are based on the common *isostructural* sulfamide host framework with the solvent molecules occupying framework cavities.

Similarities and dissimilarities of these opposite phenomena are discussed.

Elucidation of the steric and electronic effects in coordination compounds on the basis of their crystal structures

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INTRODUCTION

Understanding and explaining the factors which determine the structure (geometry) of molecules has been one of the main goals of the basic research in chemistry. For practical purposes it is convenient, but not always straightforward, to group these factors into **steric** (e.g., Pitzer strain, Baeyer strain, nonbonded interactions) and **electronic** (e.g., conjugation, hyperconjugation, donor-acceptor and π-interactions).

For structural studies chemists have at their disposal a variety of experimental and theoretical methods. The former are primarily used to collect structural data, and the latter provide ways to modeling and elucidating the individual types of effects (steric and electronic).

Coordination compounds are of particular interest in these studies since they provide many easily accessible examples of the structures which are markedly influenced by the interplay of steric and electronic factors. In addition, they offer excellent means for the systematic studies of steric and electronic effects by way of variation of their electronic and geometrical properties (e.g., by changing the central metal and donor atoms, respectively) down to "fine tuning" by varying the ligand substitution.

EARLIER WORK ON FORCE FIELD ANALYSIS

For many years, we have been developing a force field for the study of metal chelate ring conformations in coordination compounds.[1,2] The approach proved to be very successful in predicting and explaining static and dynamic conformational properties of various trigonal tris-bidentate complexes of cobalt(III) and chromium(III) with ethylenediamine,[3-5] 2,3-diaminobutane,[3,6] trimethylenediamine,[5,7-9] and 2,3-diaminopentane[6] rings. A similar approach attempted on aminocarboxylato chelates[10] yielded much less reliable results. One of the reasons for these shortcomings may stem from the complexity of the force field in

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terms of the number of parameters required for the treatment of aminocarboxylato complexes. Namely, even with the most simple potential functions[11] (consisting of bonded and non-bonded terms as the primary atom atom interactions, and with angle bending and torsional terms as the corrections) the number of individual terms increases rapidly with the introduction of new atom types (see Table 1).

Table 1: Force field complexity increases with the introduction of new atom types. Columns 2–5 show bond-stretching, angle-bending, torsional, and nonbonded terms, respectively.

Alkanes	C–H, C–C	H–C–H, H–C–C, C–C–C	C C	H···H, H···C, C···C	9 terms
Amines	N–H, N–C	N–C–H, N–C–C, H–N–C, H–N–H	C N	N···H, N···C, N···N	+10 terms
Metal-amine complexes	M N	M N C, M N H, N M–N	M N	M···H, M···C	+7 terms
Metal-glycine complexes	M O, O–C', C'–O', C'–Cα	N M O, O–M–O, M–O–C', O–C'–O', O–C'–Cα, O'–C'–Cα	M O, O–C', C'–Cα	M···O' N···O', O···C' O···Cα, C'···C' C'···Cα, C'···N O'···Cα, O'···C' O'···O, O'···O' O'···H, O···H C'···H	+27 terms
Total:	9	16	6	22	53

A comparative geometrical analysis of all published crystal structures of aminocarboxylato complexes revealed, however, an other much more important cause for the failure of a simple force field approach in these cases. It is due to the specific electronic effects that operate in compounds with two or more coordinated carboxylate groups.

STRUCTURE CORRELATION HYPOTHESIS

A relationship between the crystallographically defined static representations of molecular structures and dynamic pictures of interest to stereochemical studies is established in the form of the **structure correlation hypothesis** advanced by Dunitz[12] and his co-workers.[13]

It permits a mapping of a reaction coordinate by observing gradual static deformations of a given structure over a large variety of crystalline frameworks.

In an attempt to gain some insight into the conformational flexibility of five-membered aminocarboxylato metal chelate rings we studied[14-17] the distribution of ring conformations in the torsional subspace by the method of nonhierarchical K-means cluster analysis[18,19] on a sample of 1177 rings from 560 crystal structures extracted from the Cambridge Structural Database System (CSDS)[20] (Version 4.30). Instead of an expected continuous distribution of the points along the pseudorotational path, we observed a distinct clustering into four clusters representing two approximately enantiomeric pairs of chelate ring conformations: flattened and puckered λ and δ envelopes.[14-17] This clustering pattern is not generally correlated with the nature of the individual rings, but it appears to be the result of the mutual influence of chelate rings and possibly the other ligands. This influence is recently described [17,21,22] as anisotropic π-effect of cis- and trans-ligator pairs.

The anisotropic π-effect between two π-donors, such as two cis or trans coordinated carboxylate groups, manifests itself in a tendency of the ligand π-orbitals to adopt a mutual orientation in which the sharing of the same metal t_{2g} orbital is minimized. It is achieved through the change of the metal-oxygen torsional angle. Therefore, in cases of unfavourable mutual orientation of a pair of carboxylates, the chelate rings become puckered. Further details of this mechanism, in particular the relationship between the electronic configuration of the central metal atom and the anisotropic π-effect, is being studied in our laboratory.

NITRO COMPLEXES

The structures with the coordinated nitro groups present another example of the mutual influence of the anisotropic π-bonding ligands. Previously it has been observed[23] that the $Co-NO_2$ bond, in mixed nitro/aminocarboxylato complexes of Co(III), becomes shortened due to the trans influence of the coordinated carboxylate group

Our findings[24] indicate that this effect may be quite general. We have investigated the distribution of the $Co-NO_2$ bonds in 30 crystal structures containing 188 coordinated NO_2^- groups found in the CSDS[20] as well as in 30 "non-organic" crystal structures containing 95 coordinated NO_2^- groups obtained from Inorganic Crystal Structure Database (ICSD).[25] The following regularities may be noted. The $Co-NO_2$ bond in the structures containing organic ligands is shorter if the trans position contains COO^-, NCS^- or H_2O ligands, in comparison to the length of the $Co-NO_2$ bond which has NH_3 or another NO_2^- in the trans position. The metal NO_2 bond lengthens with the increase in the number of coordinated NO_2^- groups in both classes of nitro complexes. Again, the explanation may be sought in the trans influence of the π-bonding ligands, but the full account of the structural details

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is obtained if we accept the assumption on the existence of the **anisotropic** influence of the π-bonding ligands both in the *cis* as well as in the *trans* position.

A series of nitro–ammine complexes, $[Co(NH_3)_x(NO_2)_{6-x}]^{x-3}$ (x=0,2,3,4,5), is particularly interesting in the study of the interplay between steric and electronic effects. Molecular orbital (EHT, ZINDO, and STO-3G *ab initio*) calculations[26] clearly show the existence of anisotropic π-bonding of the M-NO$_2$ fragment, and a four-fold rotational barrier around the metal–ligand bond. Two nitro groups in either *cis* or *trans* disposition are expected to influence each other via the electronic effects. Force field calculations,[26] on the other hand, show that the steric effects (essentially the O···O non-bonded interactions) are important in the *cis*-dinitro case, and practically absent between the ligands in the *trans* position.

Therefore, it appears that two opposing effects of approximately the same order of magnitude determine the stereochemistry of a *cis*-dinitro fragment in nitro–ammine complexes, $[Co(NH_3)_x(NO_2)_{6-x}]^{x-3}$ (x=0,2,3,4), as shown in Table 2.[26]

Table 2: Steric and electronic factors influencing the
orientation of two or more *cis*-coordinated nitro groups

Steric factors:	Electronic factors:
O···O non-bonded interactions	Anisotropic *cis* π-effect
Coperpendicular NO$_2$ groups **favourable**	Coplanar $p\pi^*$-orbitals unfavourable
Coplanar NO$_2$ groups unfavourable	Coperpendicular $p\pi^*$-orbitals **favourable**

With the increase of the number of nitro groups around one metal center it becomes less possible to find their mutual orientation which is favourable both with respect to the steric and to the electronic requirements. This might be one of the reasons for the anomalous behaviour of hexanitro complexes, e.g., $[Co(NO_2)_6]^{3-}$, with respect to their spectral and thermodynamic properties.[24,26]

BIS(ASPARTATO)COBALTATE(III) COMPLEXES

Out of all the entries on aminocarboxylato complexes retrieved from the CSDS we have singled out two papers[27,28] each reporting on two crystal structures of bis(L-aspartato)cobaltate(III) complexes. These structures provide information on a total of eight crystallographically unique tridentate metal aspartato fragments. They are particularly useful in the study of concerted deformations which one of the two fused chelate rings exerts upon the other in

a conformational change. If the eight M(L-Asp) fragments are viewed in the correct order they reveal a continuous distortion pathway. Our force field calculations[29] clearly indicate that it is not possible to simulate the distortion pathway for the M(L-Asp) fragment without taking into account the mutual anisotropic π-influence of all coordinated COO^- groups in the $[M(L\text{-}Asp)_2]^-$ as a whole. Some problems that we experienced previously[30] attempting to reproduce the electronic spectra of the $[Co(L\text{-}Asp)_2]^-$ geometrical isomers were due to the neglect of these anisotropic π-effects. A progress was made in later attempts[31] to study the $[M(L\text{-}Asp)_2]^-$ isomers by a combination of the ligand field analysis and the force field analysis. On the basis of these results[31] we are currently working on an improvement of the force field for aminocarboxylato metal chelate complexes.

In conclusion I would like to emphasize that the M(L-Asp) fragment provides a very good example to define just the kind of the electronic effects that we are pursuing. The effects are not localized on the ligand in question, but are transmitted from the other ligands in the coordination sphere through the metal d-orbitals viz. through the metal–ligand bonds.

ACKNOWLEDGEMENTS

REFERENCES

1. S.R. Niketić and Kj. Rasmussen, *The Consistent Force Field*. Springer Verlag, Berlin–Heidelberg–New York, 1977.
2. S.R. Niketić, *J. Serb. Chem. Soc.* **43**: 741 (1978).
3. S.R. Niketić and Kj. Rasmussen, *Acta Chem. Scand.* **A32**: 391 (1976).
4. S.R. Niketić and Kj. Rasmussen, *Acta Chem. Scand.* **A35**: 213 (1979).
5. S.R. Niketić and Kj. Rasmussen, *Acta Chem. Scand.* **A35**: 623 (1979).
6. S.R. Niketić and F. Woldbye, *Acta Chem. Scand.* **27**: 3811 (1973).
7. S.R. Niketić and F. Woldbye, *Acta Chem. Scand.* **27**: 621 (1973).
8. S.R. Niketić and F. Woldbye, *Acta Chem. Scand.* **A28**: 248 (1973).
9. S.R. Niketić, Kj. Rasmussen, F. Woldbye and S. Lifson, *Acta Chem. Scand.* **A30**: 485 (1976).

10. S.R. Niketić, unpublished work.
11. Kj. Rasmussen, in *Strategies for Computer Chemistry*. C. Tosi (Ed.), Kluwer, Dordrecht, 1989, pp. 13-29.
12. J.D. Dunitz, in *Molecular Structure and Dymanics*. M. Balaban (Ed.), International Science Services, Jerusalem, 1980, pp. 103-128, and references cited therein.
13. H.B. Bürgi and J.D. Dunitz, *Acc. Chem. Res.* **16**: 153 (1983) and references cited therein.
14. S.R. Niketić and N. Juranić, *33rd Ann. Meeting Serb. Chem. Soc.*, Novi Sad, 1991.
15. S.R. Niketić, M. Ivković and S. Zarić, *29th Int. Conf. Coord. Chem.*, Lausanne, 1992.
16. S.R. Niketić and M. Ivković, *1st Conf. Serb. Crystallogr. Soc.*, Belgarde, 1992; M. Ivković, *Diploma Thesis*, University of Belgrade, 1992.
17. S.R. Niketić, M. Ivković and S. Zarić, manuscript in preparation.
18. T.P.E. Auf der Heyde and H.B. Bürgi, *Inorg. Chem.* **28**: 370 (1989).
19. T.P.E. Auf der Heyde, *J. Chem. Educ.* **67**: 461 (1990).
20. F.H. Allen, O. Kennard and R. Taylor, *Acc. Chem. Res.* **16**: 146 (1983).
21. D. Popović, S. Zarić and S.R. Niketić, *2nd Conf. Serb. Crystallogr. Soc.*, Belgarde, 1993; D. Popović, *Diploma Thesis*, University of Belgrade, 1993.
22. S. Zarić, *Ph.D. Thesis*, University of Belgrade, 1994.
23. R. Herak, N. Juranić and M.B. Ćelap, *Chem. Commun.* 660 (1980).
24. S. Zarić, M. Crnogorac and S.R. Niketić, *36th Ann. Meeting Serb. Chem. Soc.*, Belgrade, 1994; M. Crnogorac, *Diploma Thesis*, University of Belgrade, 1994.
25. Inorganic Crystal Structure Database, The Gmelin Institute, Frankfurt/Main (CD-ROM version), or STN International, FIZ Karlsruhe (on-line version).
26. S.R. Niketić, to be published.
27. I. Oonishi, F. Shibata, F. Marumo and Y. Saito, *Acta Crystallogr.*, **B29**: 2448 (1973).
28. I. Oonishi, S. Sato and Y. Saito, *Acta Crystallogr.*, **B31**: 1318 (1975).
29. S.R. Niketić, to be published.
30. S. Zarić, *M.Sc. Thesis*, University of Belgrade, 1990, and references cited therein.
31. S.R. Niketić and S. Zarić, *28th Int. Conf. Coord. Chem.*, Gera, 1990.

Magnetic Structures and Relationships Between Magnetic
and Crystal Structure

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In this paper neutron and x-ray diffraction studies of magnetically
ordered systems are briefly reviewed. The compatibility of crystal and
magnetic structures is emphasized. The magnetic field influence on
crystal structures is discussed. X-ray diffraction measurements of
yttrium and rare earth iron garnets are done in zero and applied magnetic
field. The magnetic field affects intensities of reflections, background
and lattice constant. A possible mechanism for the first two effects is
proposed. The lattice constant changes are ascribed to forced volume
magnetostriction and the existence of free electrons.

1. Introduction

In the science of magnetism and magnetic materials all substances
are divided in diamagnetics, paramagnetics and magnetically ordered. The
diamagnetics posses only induced magnetic moments. The paramagnetics
posses intrinsic disordered magnetic moments. In magnetically ordered
systems magnetic moments of atoms which occupy the same crystallographic
position are mutually related.

In the magnetically ordered crystals exists at least one atom with
unpaired atomic electrons. This is specific for 3d- and 4f- elements and
their compounds. The existence of magnetic order comes from the fact that
the magnetic energy:

$$E=E_{exchange} + E_{anisotropy} + E_{dipol} ,$$ (1)

is minimized by an ordered alignment of magnetic moments [1], below the
temperature at which kT overwhelms magnetic energy. These temperatures
(T_{Curie} for ferromagnetics and T_{Neel} for antiferromagnetics) can be over
1000 K (for some 3d- metals and their's oxides), but can also be very
low- around 1 K (e.g. in rare earth sesquieoxides). $E_{exchange}$ is larger

and often much larger than the $E_{anisotropy}$. The contribution of E_{dipol} is usually, except at very low temperatures, negligible.

The determination of magnetic structure (i.e. determination of size and orientation of magnetic moments respect to the crystal axis) is the first task in the investigation of magnetically ordered crystals. This task can be solved by: classical magnetic measurements of magnetization, magnetic anisotropy and magnetostriction; Moessbauer spectroscopy; x-ray diffraction of synchrotrone radiation and neutron diffraction. The most usual opinion is that all these tools are rather limited in comparison with the neutron diffraction [1,2].

2. Neutron diffraction at magnetically ordered systems

Nuclear and magnetic scattering are typical for neutrons. Neutron having magnetic moment $-1.913\mu_B$ interacts with magnetic moments of crystals. The amplitude of nuclear scattering is given with:

$$F^N = \sum_\nu b_\nu \exp[2\pi i(hx_\nu + ky_\nu + lz_\nu)], \tag{2}$$

where summing takes into account all atoms (of atomic amplitude b_ν) with fractional coordinates (x_ν, y_ν, z_ν) in elementary cell.
The amplitude of magnetic scattering is given with:

$$F^M = \sum_\nu f_\nu^M M_{hkl,\nu} \exp[2\pi i(hx_\nu + ky_\nu + lz_\nu)], \tag{3}$$

where summing takes into account all magnetic atoms (with magnetic form factor f_ν^M) in elementary cell. Vector $M_{hkl,\nu}$ depends on the scattering vector e_{hkl} and magnetic moment m_ν:

$$M_{hkl,\nu} = m_\nu - (e_{hkl}m_\nu)e_{hkl} \tag{4}$$

The structure factor (for nonpolarized neutrons) is the sum of nuclear and magnetic structure factors [1,2].

Thousands of magnetic structures have been resolved by the use of neutron diffraction data. The simplest structures are collinear: ferro-, antiferro- and ferrimagnetic. The ferro- and simple collinear antiferro- appear only if magnetic atom occupies only one Wyckoff's position.

9

Ferrimagnetic structures exist if magnetic atoms are distributed over two or more positions. Noncolinear structures usually appear in highly anisotropic systems. To this group belong weak ferromagnetic, umbrella, multiaxial and helicoidal structures [3].

Tremendous majority of magnetic structures are solved on the basis of the paramagnetic space group [3]. These solutions are nonexact because neglect the symmetry of magnetic moment which, strictly speaking, must be compatible with the symmetry of local position. The point group is a subgroup of the group of magnetic moment (a consequence of Curie's principle). Second, the lowering of the symmetry corresponds to the phase transition between para and ordered magnetic phase (according to Landau's theory).

The requirement for the exact solution of magnetic structures (i.e. compatibility of the local symmetry and the symmetry of the magnetic moment) leads to the requirement for the exact solution of crystal structures (i.e. compatibility of magnetic and crystal structures) in ordered magnetic phases.

3. X-ray diffraction at magnetically ordered systems and the magnetic field influence on crystal structure

X-rays interact with charge and magnetization density. The ratio of the charge scattering to the magnetic scattering intensity can be several orders of magnitude [4]. From that reason magnetic scattering can hardly be visible if the usual x-ray reflection overlaps magnetic reflection (ferromagnetics and ferrimagnetics). On the other hand, the appropriate choice of samples (e.g. antiferromagnetic NiO [5] and spiral Ho [4]) makes magnetic x-ray scattering observable with a synchrotrone and, in good running conditions, with rotating anode source.

Usual x-ray diffraction measurements at magnetically ordered systems are performed to study magnetoelastic effects. Temperature dependence of lattice parameters of ferrimagnetic $Re_3Fe_5O_{12}$ was investigated several times below room temperature [6] (and references therein). A general conclusion can be drawn from all of these measurements. At room temperature ferrimagnetic garnets posses "cubic metric and rhombohedral symmetry" [7]. The rhombohedral structures, space group $R\bar{3}$, were found at low temperatures [8]. The visible effect- increase of rhombohedral angle

with the lowering of temperature can be described as diffuse phase transition. Strictly speaking this transition appears at T_c and only instrumental resolution of diffractometers, which is poor in the comparison with the size of effects, does not allow following of the effect at immediately below T_c.

There are no many data on magnetic field influence on crystal structure. Workers in the field usually study changes of crystal structure parameters e.g. lattice parameter and it's thermal evolution.

X-ray diffraction experiment has been done on Dy-4%Y alloy using superconducting electromagnet. The applied field changes volume fraction of coexisting ferro and spiral magnetic structures. The corresponding crystal structure in the spiral phase is hexagonal which distorts to the orthorhombic in ferro state [9,10].

4. X-ray diffraction at rare earth garnets in magnetic field

In order to investigate the magnetic field influence at crystal structure of magnetically ordered systems yttrium and rare earth iron garnets are chosen. Above T_c, which is about 560K for $Y_3Fe_5O_{12}$ and $Re_3Fe_5O_{12}$, these garnets crystallize in the space group Ia3d. The ferri ions occupy 16a and 24d positions. Y^{3+} (Re^{3+}) and O^{2-} occupy 24c and general 48f positions, respectively.

Yttrium and rare earth iron garnets of the chemical formulae $Y_3Fe_5O_{12}$ and $Re_3Fe_5O_{12}$ (Re=Sm, Gd, Tb, Dy) are synthesized by coprecipitation of starting compounds (Fe_2O_3 and Y_2O_3 purity 99.99%) followed by sintering and resintering at 900 and 1380°C, respectively.

Diffraction measurements were done by using $CuK_{\alpha 1,2}$ radiation (40 kV and 80mA) in 2θ region $9^{\circ}-135^{\circ}$. The data were collected in steps of 0.05° in 2θ and measurements lasted about 20 hours for each sample. In the second run same samples were measured in applied magnetic field B=0.1T, which was oriented along the scattering plane.

Main differences between the data obtained in the fields B=0 and B=0.1T are shown in Table I. The Rietveld's refinement does not show any significant differences between other crystal structure parameters.

Table I

Diffraction data and lattice constants of ReIG

Garnet/	scale factors	backgrounds	lattice constants [Å]	
	ratio	ratio	a(B=0)	a(B=0.1T)
YIG	2.2	2.6	12.3816(2)	12.3854(6)
SmIG	2.3	2.5	12.5319(4)	12.5378(6)
GdIG	1.9	3.8	12.4779(6)	12.4807(6)
TbIG	1.1	0.9	12.4443(6)	12.4433(6)
DyIG	2.9	2.9	12.4097(5)	12.4128(6)

Scale factors ratio is defined as: sf(B=0)/sf(B=0.1T). Backgrounds ratio is defined as: total bckg(B=0)/total bckg(B=0.1T)

The magnetic field affects total intensity of reflections and total intensity of background. We propose a possible mechanism of this effect. The existence of an applied magnetic field causes appearance of an electric field. The x-rays produce free electrons in investigated samples. Moving of free electrons in electric and magnetic field, due to the Lorentz's force, makes their recombination with ions more difficult. The existence of enlarged number of free electrons changes electron density of the sample (which we see as the structural changes) and affects background. Except above mentioned reasons for the changes of crystal structure of YIG and ReIG, we also note: i) the magnetic field orients domains; ii) the forced volume magnetostriction (and maybe existence of free electrons) change lattice parameters, iii) the depth of x-ray penetration can be changed in the magnetic field.

5. Conclusion

Up to now investigations of crystal and magnetic structures were mainly led separately. The most researchers try to resolve magnetic structures by simply adding magnetic structure on the "known" crystal structure, even if it is very well known that magnetic structure lowers the symmetry of crystal structure. The exact knowledge of crystal structures of magnetically ordered compounds can be very great help in

magnetic structures investigations.

The investigations of crystal structure and it's parameters in magnetic field is not a popular technique and not much is known about it problem. The experiments done on YIG and ReIG show strong magnetic field dependence of x-ray scattering and crystal structure parameters.

References
1. W.Prandl, 113-149, in Neutron Diffraction ed. H.Dachs, Springer-Verlag, Berlin 1978.
2. Y.A.Izymov, W.E.Naish, R.P.Ozerov, Neitronografiia magnetikov, Atomizdat, Moskva 1981.
3. A. Oles, F.Kayzar, M.Kucab, W.Sikora, Magnetic Structures Detrmined by Neutron Diffraction, PWN, Warszawa-Krakow, 1976.
4. D.Gibbs, D.E.Moncton, K.L.D'Amico, J.Appl.Phys.57(1985)3619.
5. F.De Bergevin, M.Brunel, Phys. Lett. 39A (1972) 141.
6. M. Guillot, D. Rodic and M.Mitric J.Appl.Phys., 73-77(1993) 6304.
7. E.F.Bertaut, IEEE Trans.Magn., 17(1981)2520.
8. R.Hock, H.Fuess, T.Vogt, M.Bonnet, J.Sol.St.Chem.84 (1990) 39. 9. K.Tayima, N.Suzuki, K.Oguchi, Jap.J.Appl.Phys. 29 (1990)986.
10. K.Oguchi, K.Tayima, Y.Shinoda, J.Phys.Soc.Jap. 60(1991)2371.

THE CRYSTAL AND MOLECULAR STRUCTURE OF 3α,28:6α,7α-DIEPOXY-2--OXA-5α,10α-CHOLESTANE, $C_{27}H_{44}O_3$

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During the investigation of nucleopphilic substitution of $6α,7α$ epoxydes (1) the compound $3α,28:6α,7α$-diepoxy-2-oxa-5α,10α-cholestane has been synthesized. Since NMR spectra interpretation has ailed to recognize molecular structure in details, X-ray crystal structure investigation has been performed in order to characterize its structural properties.

Crystal data: monoclinic, a=37.970(9) Å, b=5.991(2) Å, c=10.939 Å, $β$=94.38(8)°, space group C2, Z=4, M_r =416.58, D_x=0.672 g/cm^3 , V=2481(3) Å^3 , $λ$(MoK$_α$)=0.71079 Å, $μ$(MoK$_α$)=0.7 cm^{-1} , F(000)=932.

The crystal structure has been solved by direct methods and refined by full-matrix least-squares to (at this moment) R=0.111.

The geometry of the molecule as well as conformations of steroidal nucleus and side chain group seems reasonable.

(1) Bogdan Šolaja and Ljiljana Došen-Mićović, Transformations of some steroidal lactones and study of nucleophilic substitutions of $6α,7α$ epoxides, J. Serb. Chem. Soc., 54 (12), 657-669 (1989).

AN UNUSUAL HYDROGEN BOND NETWORK IN CRYSTAL PACKING OF 3-MET-
HOXY-16-OXIMINO-17𝛼-BENZYL-17𝛽-HYDROXY-ESTRA-1,3,5(10)-TRIENE

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ABSTRACT. The asymmetric unit of the title compound, 3-metho-
xy-16-oximino-17𝛼-benzyl-17𝛽-hydroxy-estra-1,3,5(10)-triene,
C26H31NO3, contains two molecules (I and II), which differ in
the orientations of the C(3) methoxy groups. 17-Hydroxy and
16-oximino moieties are involved in the intramolecular N...H-
-O hydrogen bonds. At the same time, molecules I and II are
linked by the additional intermolecular N(I)...H-O(2II) and
O(3I)-H...N(II) hydrogen bonds forming dimers. These dimers
form further columns along a-axis through O(2I)...H-O(3II)
intermolecular hydrogen bonds.

         The hydrogen bond network causes a difference of
bond and torsion angles of 𝛽-hydroxy oximino moieties betwe-
en two symmetricaly independent molecules. This has been con-
firmed by molecular mechanics calculation on individual mole-
cules I and II, leading to the same geometries for either mo-
lecule in their energy minimum state.
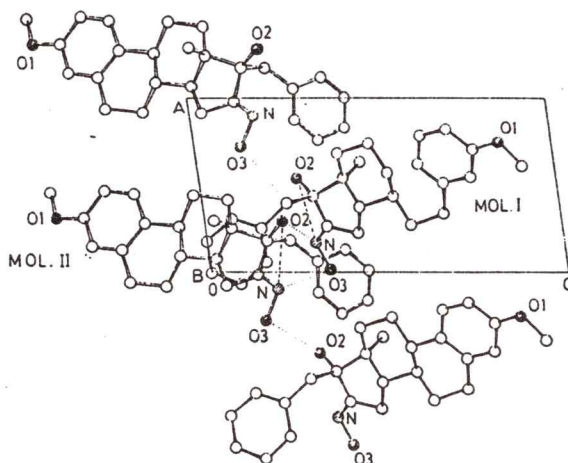
ISOSTRUCTURALISM OF THE STEROID COMPOUNDS OF CORTISON DERIVATIVES

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Isostructural pairs or groups of compounds usually have very similar crystal unit cell parameters and belong to the same space group [1]. In order to test isostructuralism, we have compared the crystal structures of four compounds of the steroid type having the general bruto formula $C_{21}H_{28+s}O_{3+t}X$ ($s = 0, 1, 2, 6$ $t = 0, 2$ $X =, F$) and rather similar unit cell parameters (compound I: $a = 10.040(2)$Å, $b = 23.649(2)$Å, $c = 7.784(2)$Å, $P2_12_12_1$ Fig.1).
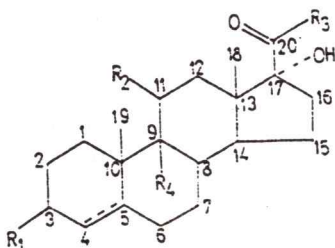
R_1	R_2	R_3	R_4	4 − 5
I cortisone $C_{21}H_{28}O_5$				
O	O	$CH_2 - OH$	H	==
II 17α-hydroxyprogesterone $C_{21}H_{30}O_3$				
O	H_2	CH_3	H	==
III tetrahydrocortysol $C_{21}H_{34}O_5$				
OH	OH	$CH_2 - OH$	H	−−
IV 9α-fluorocortisol $C_{21}H_{29}O_5F$				
O	OH	$CH_2 - OH$	F	==

Comparing the coordinates of the atoms belonging to the basic skeleton of the steroid $C1 - C19$, a possibility was noticed the transformation of the coordinates of the atoms of compound I into the coordinates of the cooresponding atoms in the compound IV. In order to verify the isostructurality, we have taken the coordinates of the atoms of the compound I as the initial parameters for $N = 1867$ observed reflexes measured on the crystals of the compound IV. We have performed three cycles of anisotropic refinment (SHELX76) and the difference Fourier map was calcualted. The decrease of R-factora and the appearance of the maxima in the difference Fourier map, whose position corresponds to the coordinates of F atoms from the compound IV, have confirmed the isostructurality of the studied compounds.

In order to test the origins of the isostructurality, we have performed the analysis of the molecular packing for all four compounds. Large similarity of packing was noticed for the compounds I, II i IV. The established isostructurality between the compounds I and IV could be ascribed to the same type of strong intermolecular hydrogen bond ($O17 - H17...O21, O21 - H21...O3$) while in the compounds II and III completely different network of hydrogen bonds is formed.

[1] Kalmán A., Gy.Argay, D.Scharfenberg-Pfeiffer, E.Höhne, B.Ribar, Acta Cryst.,B27,68-77,(1991).

INFLUENCE OF CRYSTALLIZATION CONDITIONS OF Al ON THE SHAPE OF THE CRYSTALLIZATION FRONT

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Properties and quality of a crystal depend on crystallization conditions very much. The study of dependence of the crystallization front shape on the crystallization conditions in the Al - (Zn, Fe, Si, Cu) system is presented in this paper.

Set of experiments was done using Bridgeman's normal solidification method (vertical system). The ampoule with sample was moved upwards and downwards in the vessel. The solidification rate was considered to be equal to the sample velocity. The experiments were carried out within a wide range of growth rates from 3.61×10^{-5} cm/s to 8.71×10^{-3} cm/s. Two different initial solute concentrations were used.

The increment in the growth rate changes the crystallization front shape from plane to cellular. Further increase in the crystallization rate caused the crystallization front shape transition from cell to dendrite.

The quantitative criterion was used to determine the critical crystallization rate value for plane to cellular front shape transition. Minimal crystallization rate used in series I resulted in planar crystallization front shape. Increase in growth rate caused the cellular growth. The development of cell structure up to transition to dendritic growth was studied in series II of experiments.

A METHOD FOR PREPARATION CRYSTALS IN A CHAMBER FURNACE

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In order to prepare monocrystals of group compounds [1], in a laboratory chamber furnace, we have designed an apparatus. Its main parts are: an electroresistant chamber furnace, a heat exchanger, crucible, outer crucible and a continuously changeable transformer. The lower part of the crucible is a capillary which is considered to select one of the spontaneously formed grains from the other ones as to develop into a monocrystal [2]. The procedure involves firstly an increase of the voltage until the substance in the crucible is completely melted. Then, an air stream is let to flow through the heat exchanger. At the beginning the air flow is weak but it is gradually increased so that the solidification front, which starts at the outer crucible bottom, moves upwards up to reaching the surface of the melt after several hours.

The rate of crystallization in each crucible can be adjusted by changing the cross-section of the air flow, which allows a simultaneous crystallization of several substances at different rates.

REFERENCES

[1] B. Čabrić, B. Žižić, M. Lj. Napijalo: Synthesis and crystallization of $BaNi_2(PO_4)_2$. J. Cryst. Growth, 60, 169 (1982).
[2] K.-Th. Wilke, J. Bohm: Kristallzüchtung, Verlag, Berlin 1988, p. 591.

RELATIONSHIP BETWEEN UNIT CELL PARAMETERS AND COMPOSITION OF TERNARY

SPINELS $Zn_xM_ySb_zO_4$ (M = Cr, Mn, Co, Ni)
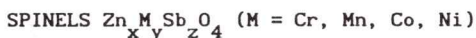
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Spinels are a large group of natural and synthetic compounds with very diverse application in science and technology (Cr production, pigments, magnetic materials, catalysts, varistor ceramics). Well known structure of spinels (A)[B]O_4 consists of approximately cubic closest packing of O^{2-} ions and cations in tetrahedral, (A), and octahedral, [B], positions. Different kind of substitutions are possible in (A) and [B] sites.

The spinels with formula $Zn_xM_ySb_zO_4$ (M = Cr, Mn, Co, Ni) have been prepared by solid state reaction at about 1100°C from appropriate oxides. The samples are examined by X-ray powder diffraction technique on a Philips PW 1710 automatic diffractometer using monochomatized Cu Kα radiation.

The unit cell parameters of prepared spinels linearly depend on percentage of transition metal, M. The linear equations obtained by regression analysis are follows (r is the correlation coefficient):

for M=Co: $a(\text{Å}) = -0.015(3) \cdot y + 8.595(2)$ (y≤0.933; r=0.931)

for M=Ni: $a(\text{Å}) = -0.056(8) \cdot y + 8.595(4)$ (y≤0.933; r=0.974)

for M=Mn: $a(\text{Å}) = -0.092(3) \cdot y + 8.594(9)$ (y≤0.500; r=0.999)

for M=Cr: $a(\text{Å}) = -0.134(4) \cdot y + 8.594(2)$ (y≤0.778; r=0.998)

In order to check the stated dependence some spinels of more complex composition and general formula $Zn_xM'_yM''_wSb_zO_4$ have been prepared in the same way. In Table 1 the experimental unit cell parameters of these spinels are given with the values calculated by the assumption that the contribution of each ion is additive. The agreement between experimental and calculated values is good. It gives the opportunity to predict the unit cell parameters of even more complex spinels.

Table 1. The unit cell parameters of spinels $Zn_xM'_yM''_wSb_zO_4$.

Spinel formula	$a_{obs.}$ (Å)	$a_{calc.}$ (Å)
$Zn_{1.633}Co_{0.350}Ni_{0.350}Sb_{0.667}O_4$	8.5693(9)	8.5700
$Zn_{1.815}Cr_{0.389}Mn_{0.389}Sb_{0.407}O_4$	8.5115(8)	8.5069
$Zn_{1.724}Cr_{0.387}Co_{0.350}Sb_{0.537}O_4$	8.532(1)	8.5375
$Zn_{1.676}Cr_{0.181}Ni_{0.537}Sb_{0.606}O_4$	8.5370(7)	8.5403
$Zn_{1.724}Cr_{0.389}Ni_{0.350}Sb_{0.537}O_4$	8.5190(4)	8.5230
$Zn_{1.733}Cr_{0.596}Ni_{0.163}Sb_{0.468}O_4$	8.4991(6)	8.5057

In accordance with our previous results (D.Poleti, D.Vasović, Lj.Karanović, Z.Branković, J.Solid State Chem., in press) the same cation distribution is expected in all prepared spinels, i.e. the tetrahedral sites are occupied exclusively by Zn^{2+} ions.

THE COMPARISON OF DIFFERENT COMPUTER PROGRAMS FOR RIETVELD ANALYSIS OF X-RAY POWDER DIFFRACTION PATTERNS FOR SPINEL $Zn_x M_y Sb_z O_4$ (M=Mn,Cr,Co,Ni)

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The existence of different computer programs for the Rietveld analysis of X-ray powder diffraction patterns reqaires a) the comparison of programs and consideration of conveniences and unconveniences of them, b) the investigation of different strategies in crystal structure refinement and c) the estimation of accuracy and spread of values found by different programs. The structure of spinel $Zn_{1.4}Ni_{0.933}Sb_{0.667}O_4$ has been refined using programs WYRIET-2, DBWS-9006, LHPM8-93.06 and FULLPROF-2.2 (PC-versions).

Crystal data and X-ray powder diffraction data are listed in Table 1 and R-values obtained with different versions of Rietveld's program for rough and smoothed data in Table 2 .

Table 1. Crystallographic data for spinel $Zn_{1.4}Ni_{0.933}Sb_{0.667}O_4$

Diffractometer	PW1710
X-ray tube	Cu LFF 40kV 30mA
Wavelenght ($\overset{o}{A}$)	1.5405, 1.5443
Profile range ($^{o}2\theta$)	10-120
Step width (^{o})	0.02
Step time (s)	10
Peak range (number of FWHM)	6.3
Number of observation	5500 (4608)[*]
Space group	Fd3m
a ($\overset{o}{A}$)	8.5368(1)
V ($\overset{o}{A}{}^3$), Z	622.14(3), 8
M_r	291.50
D_x (g/cm^3)	6.222
$F(000)$	1073

[*] Wyriet-2

Tabela 2. Agreement indices for spinel $Zn_{1.4}Ni_{0.933}Sb_{0.667}O_4$

	WYRIET-2[*]		DBWS-9006		LHPM8-93.06		FULLPROF-2.2	
	RD	SM	RD	SM	RD	SM	RD	SM
R_{exp}	5.59	5.61	5.77	5.78	5.76	5.77	5.76	5.77
R_p	13.57	14.11	9.99	8.26	10.57	8.96	9.94	8.29
R_{wp}	17.75	18.63	12.92	10.84	15.25	13.57	12.90	10.9
R_B	7.22	7.23	4.55	4.28	3.93	3.57	4.63	4.12
R_F	4.04	3.94	2.95	3.02	2.23	2.17	3.52	3.61
N	17	17	17	17	17	17	18	18

[*] Smoothed data

INVESTIGATION OF THE GEOMETRY OF DINITROBIS(AMINOCARBOXYLATO)COBALTATE(III) ISOMERS ON THE BASIS OF THE KNOWN CRYSTAL STRUCTURES

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Dinitrobis(aminocarboxylato)cobaltate(III) complexes have been synthesized with various amino acids (1). Only four out of the five theoretically possible geometrical isomers were isolated irrespective of the amino acid used in any of the syntheses. For the four isolated geometrical isomers crystal structures are known with several amino acids.

Recently the existence of the electronic π-effect was described. This effect was shown (2) to account for the difference in the conformations of the five-membered metal-aminocarboxylato chelate rings as well as for the differences in the thermodynamic stabilities.

In this work the electronic π-effect is demonstrated on the variations in metal-ligand bond lengths in the crystal structures of dinitrobis(aminocarboxylato)cobaltates(III). The position and mutual orientations of the π-bonding ligands were considered. due to the anisotropy of the π-bond between carboxylato oxygen or the nitrogen from a nitro group and the cobalt atom, the M-O and M-N bonds are influenced by the ligand in the *trans*-position. Moreover, if the *trans*-ligand is π-bonding, then its orientation also influence the corresponding metal-ligand bond length.

(1)   M.B. Ćelap, D.J. Radanović, T.I. Nikolić and T.I. Janjić, *Inorg. Chim. Acta*, **2**, 52 (1968)

(2)   D. Popović, S. Zarić and S.R. Niketić, *Second Conference of the Serbian Crystallographic Society*, Belgrade, 1993.

SYNTHESIS AND CRYSTAL STRUCTURE OF Cu(II) COMPLEX WITH ACETONE NAPHTOYLHYDRAZONE HL, [Cu(HL)(L)NO3]·C2H5OH

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By the reaction of hot E_t/Me_2CO solutions of Cu(II) nitrate and acetone 1-naphtoylhydrazone (HL), mixture of pale (in the excess) and dark green crystals was obtained. On the basis of x-ray structure analysis it has been found that pale green crystals have $trans,trans[Cu(HL)_2(NO_3)_2]$ configuration (1).

In this communication results of the crystal structure analysis of dark green crystals having formula $[Cu(HL)(L)NO_3]C_2H_5OH$, as determined by the analysis itself, are presented.
Fundamental crystallographic data are: orthorhombic, a=14.335(4) Å, b=20.695(5) Å, c=10.445(3) Å, space group Pan2$_1$, V=3099(1) Å^3, M$_r$=417.87, $\lambda(MoK\alpha)$=0.71073 Å, $\mu(moK\alpha)$=14.50 cm^{-1}.

The structure was solved by heavy atom methods and refined by full-matrix least squares to R=0.0452 and R$_w$=0.0501.

The most interesting characteristics of the structure of complex are represented by the shape of the coordination polyhedron around the metal atom and by the electron charge distribution in the molecule. The coordination number of the central atom may be described by 5+1, where the first coordination sphere is built up by pairs of oxygen and nitrogen atoms belonging to two five-membered chelate rings and the oxygen atom from nitrate group. The second coordination sphere is represented by second oxygen atom belonging to the nitrate group. The polyhedron is strongly deformed geometrical frame, the deformation being partialy recognized as steric influence of other groups of atoms in the molecule.

Five membered chelate rings are almost planar, but there are evident differences of their corresponding bond lengths. These differences are ascribed to deprotonation in one of chelate rings, so the commencing dilemma if we are dealing with Cu(II) or Cu(I) complex has been resolved at the final stage of crystal structure analysis and confirmed by measurements of magnetic susceptibility of the powdered substance.

(1) R.Herak, B.Prelesnik and V.Leovac, The Crystal Structure of Dinitro-bis(acetone 1-naphtoylhydrazone)copper(II), II Conference of the Serbian Crystallographic Society, Belgrade 1993, p.41.

CRYSTAL AND MOLECULAR STRUCTURE OF THREENUCLEAR COMPLEX
$Cu_2^I Cu^{II}(HL)_2 Br_4$ ($HL = 1$ - naphtoylhydrazon acetone)

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Monocrystals of the complex were obtained by the slow evaporation of the etanol-acetone solution of $CuBr_2$ and 1-naphtoylhydrazon acetone. Dark green prismatic crystals belong to triclinic system $P\bar{1}$ with unit cell parameters $a = 7.510(1)$Å, $b = 9.700(1)$Å, $c = 11.570(1)$Å, $\alpha = 99.38(1)°$, $\beta = 106.20(1)°$, $\gamma = 91.49(1)°$, $Z = 2$, $V = 796.4(2)$Å³, $D_c = 2.007 Mgm^{-3}$, $M_r = 481.40$, $F(000) = 467$.

The structure was solved by the direct method using the program SHELXS86 and refined by SHELX76 til the final R factor $R = 0.0509$, $R_w = 0.0411$, $w = 2.3039/\sigma^2(F)$, $N = 2954$, $NP = 237$, $S = 0.318$.

Cu^{II} has octahedral environment of two bidentat (N, O) molecules of 1-naphtoylhy-drazon acetone in the equatorial plane and two bromide ions in axial positions. The atoms of Cu^I are located in the trigonal planar environment built by two bridging bromids which relate connect Cu^I atoms and the brom ion from the octahedral envi-ronment of Cu^{II} (Fig.1).
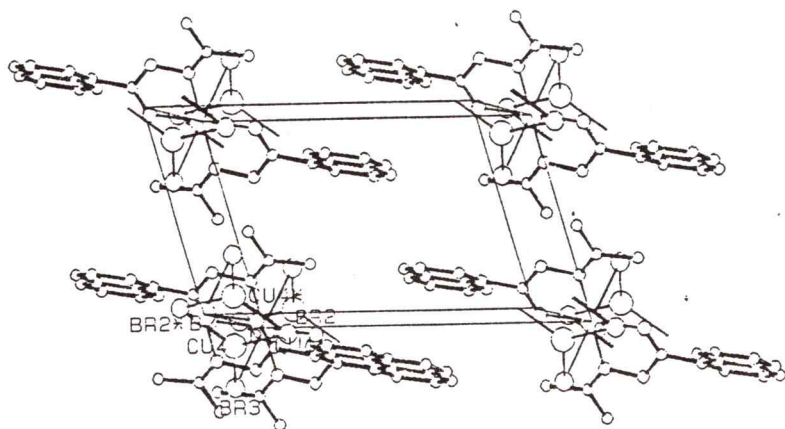
Infinite chains along crystallographic b direction are formed. The chains are connected by weak Van der Waals contacts ($Br3...N2^* = 3.427(5)$Å, $Br3...H2^* = 2.829(72)$Å,*) $-1 + X, Y, Z$) and form layers parallel to ab plane.

COMPUTING AID DRUG DESIGN: 3-HYDROXY-18-METHYL-17-OXOESTRA-
-1,3,5(10)-TRIEN-16-ONE

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In order to obtain estrogen type compounds with antiestrogen activity, we started with the exemination of compounds with the hetero D-ring and their D- and C,D-seco derivatives. Namely, it is known that estrogen type estranes with D-hetero and D-seco ring loose estrogen activity, while very few data concerning their antiestrogen activity are available. To simplify the sinthesis of compound for which the antiestrogen behaviour could be supposed (according to our assumption the compound should have the conformation of tamoxifen) we used computing aid drug design. Starting with the crystal structure of 3-hydroxy-18-methyl-17-oxoestra--1,3,5(10)-trien-16-one some D- and C,D-seco derivatives of this compound are designed by the molecular mechanics and then their conformations compared to the tamoxifen conformation.

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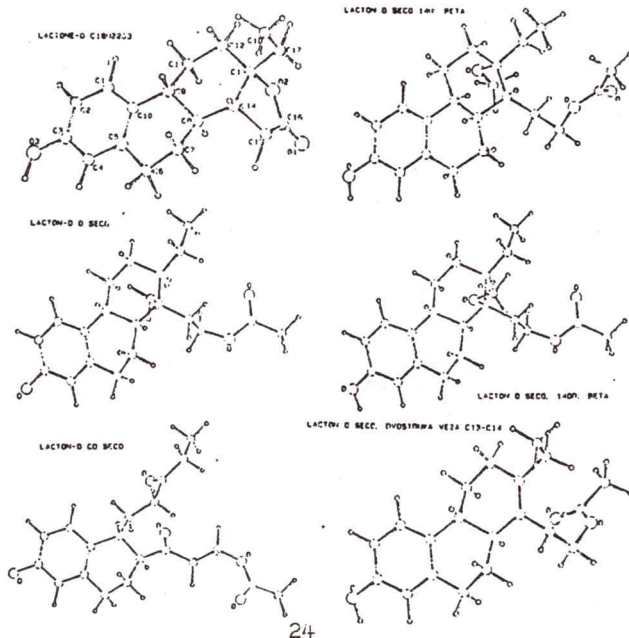
AN INDICATOR FOR THE ADJUSTMENT OF AN X-RAY BEAM

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In order to optimize centering and the adjustment of cameras, goniometer or other instruments, an indicator of X-rays is designed.

The principle of this indicator is based on a known property of zinc sulphide doped by copper (1:10000) to produce the light depending on intensity of X-rays.

A piece of ZnS fluorescent screen is mounted in front of a CdS photoresistor, whose resistance depends on light and both, the screen and photoresistor are set in a black foil or paper. An amplifier by FE transistor is set close to the photoresistor. This transistor amplifier is a part of a bridge, which measures the resistance by an analogue microampermeter up to 100 μA (Fig. 1.).

The use of analogue instrument instead a fluorescent screen for cameras, goniometer and other instruments for adjustment to the X-ray source is much more convenient then the adjustment performed by observation an intensity of a spot on the fluorescent screen in darkness. In the same time, it is less dangerous.
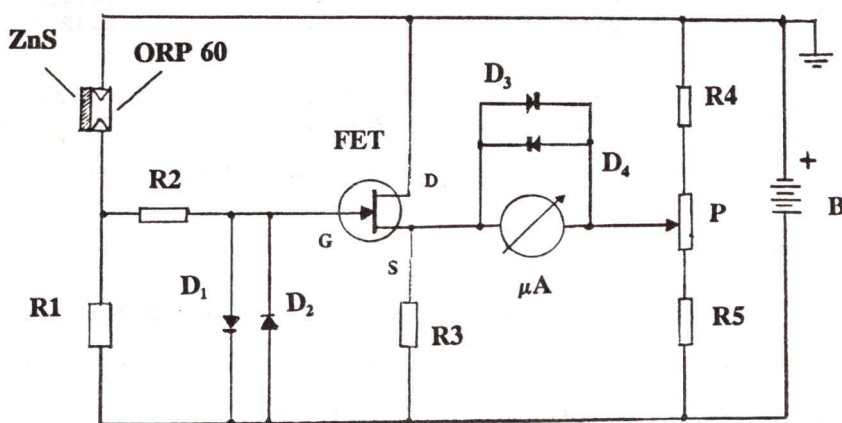

Fig. 1. Circuit diagram of an X-ray indicator

THE UNIT CELL FOR THAUMASITE FROM VLAOLE VILLAGE VICINITY (EAST SERBIA)

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For **thaumasite**, $CaCO_3.CaSiO_3.CaSO_4.14.5\ H_2O$ · the rare mineral found in E. Serbia, described by S. Janjić et al (1) the hexagonal unit cell was calculated.

From X-ray diffraction powder pattern up to $2\theta = 90^0$ of relatively pure mineral 77 reflections was collected. Only six reflections whose intensities was less than 1% could not be indexed to the thaumasite reflections. The refinement of the unit cell was calculated by a least square method from all of rest 71 reflections. Some starting indexes was used from the literature.

Comparative values for the unit cell for thaumasite from Vlaole and data from literature, are given in the table below:

	Vlaole	Lit. 3	Lit. 2
$a_0(\text{Å})$	**11.038(2)**	10.992	11.03
$c_0(\text{Å})$	**10.384(3)**	10.311	10.40
$V_0(\text{Å}^3)$	**1095.6(6)**	1078.9	1095.8

Small differences between various thaumasites derives on differences in chemical compositions. Some of this in the literature contains Na_2O, K_2O, Cl, TiO_2 and MgO; but thaumasite from Vlaole contains more Al_2O_3 than others.

References:

(1)   Janjić, S., Živković, P. & Bugarski, P.
      Bull. Mus. Hist. Natur. **36**, 17-22, (1981) Belgrade

(2)   Knill, Min. Magaz. **32**, 416 (1960); JCPDS card # 25-128

(3)   Font-Alba, Min. Magaz. **32**, 657 (1960)

(4)   "Minerali" Tom III. Taumasit; Nauka, (1972) Moskva

Relations of Structure and Magnetic Properties in
Solid Solutions of Yttrium-Erbium Sesquioxides

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The solid solutions of yttrium-erbium sesquioxides are diluted magnetic semiconductors (DMS) of $Y_{2-x}Re_xO_3$ type (Re=rare earth). Some new properties of these materials are important for fundamental researches as well as in applications.

The knoledge of crystal structure is the basis for understanding magnetic properties of the diluted magnetics. Some structure and magnetic properties of $Y_{2-x}Er_xO_3$, mutually related, are given in the present work.

The crystal structure of $Y_{2-x}Er_xO_3$ were refined by the Rietveld method in the space group Ia3 and structure type $C-M_2O_3$. The refined values of occupancies show random distribution of Er^{3+} ions over two nonequvalent crystallographic sites, 8b and 24d. This type of distribution was confirmed by magnetic measurements - the gram ion susceptibilities at room and liquid nitrogen temperature are independent of magnetic ion concentration.

The random crystallographic distribution and random distribution of magnetic ions in the frame of both cation sites would lead to the linear behaviour of Curie-Weiss paramagnetic temperatures versus magnetic ion concentration-$\theta(x)$. The observed nonlinear $\theta(x)$ dependence is a consequence of magnetic ions clusterisation in both cationic sites (microscopic distribution) for $x \leq 0.40$.

Crystalochemistry data enables understanding of magnetic moment values and superexchange interactions. Magnetic susceptibility data, together with obtained types of magnetic ions, distributions and theirsurrounding give a possibility for the calculation of the effective exchange integral.

References:
Antić B., Mitrić M. and Rodić D., submitted in J.Mag.Mag.Mat.
Rodić D., Antić B. and Mitrić M., ICM'94 Abstracts, Warsaw, 22-26 August 1994, p.749.

THE STRUCTURE CHANGES OF MIXED TERBIUM-YTTRIUM GARNET $TB_{2.5}Y_{0.5}FE_5O_{12}$ IN APPLIED MAGNETIC FIELD

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The x-ray diffraction experiments on mixed terbium-yttrium garnet $Tb_{2.5}Y_{0.5}Fe_5O_{12}$ were done in applied magnetic field $B \cong 0.1$ T. Before the x-ray measurements in the magnetic field the domains were oriented in the same field. The intensities of reflections and background strongly depend on the orientation of the applied field against scattering plane. The positions of reflections also show dependance of the orientation of the applied field. The observed phenomena points to the vector's nature of the structure amplitude and the lowering of the symmetry in the magnetic field.

1. Introduction

Above T_c, which is about 560K for $Y_3Fe_5O_{12}$ and $Re_3Fe_5O_{12}$, garnets crystallize in the space group Ia3d. At room temperature ferrimagnetic garnets posses cubic metric and rhombohedral symmetry [1]. The last statement comes from the following facts: i) below T_c magnetic structure is ferrimagnetic, colinear, and all magnetic moments are oriented along body diagonal (in pseudo cubic cell); ii) according to the Curie's principle and the Landau's theory of phase transitions, below the phase transition at T_c the symmetry of garnets is lower (rhombohedral) than in the paramagnetic phase; iii) all known diffraction measurements of Y(Re)IG at room temperature and above it show presence of (pseudo) cubic structure. The rhombohedral structures, space group $R\bar{3}$, were found at low temperatures (e.g. [2]). Up to our best knowledge, only TbIG has been described once in $R\bar{3}$ group at room temperature but with lattice constants and atomic parameters which can be recalculated to correspond to the cubic space group Ia3d [2].

The magnetostriction is mechanism which lowers the symmetry of magnetically ordered phase. In order to see magnetostriction effects in the mixed terbium-yttrium iron garnet $Tb_{2.5}Y_{0.5}Fe_5O_{12}$, we have measured

x-ray diffraction in applied magnetic field of 0.1T.

2. Experimental

$Tb_{2.5}Y_{0.5}Fe_5O_{12}$ is synthesized starting by coprecipitation of materials which corresponds to the formula: $2.5Tb_2O_3 \cdot 0.5Y_2O_3 \cdot 5Fe_2O_3$ by the method described elsewhere [3]. The obtained mixture was pressed into pellets under the pressure of $1.5ton/cm^2$ and sintered at 900^0C for 10 hours. The obtained product was crashed, pressed under the same pressure and finally resintered at and 1380^0C for 12 hours.

In order to allow free orientation of domains in the magnetic field $Tb_{2.5}Y_{0.5}Fe_5O_{12}$ sample was put in distilled water to form mud. This mud was entered in magnetic field of 0.1T and than dried at 150^0C. The line forces of the field passed through the entire sample.

Diffraction measurements on the sample in the field were done by using $CuK_{\alpha1,2}$ radiation (40 kV and 80mA) in 2θ region 9-86°. The data were collected in steps of $0.05°$ in 2θ and measurements were lasted 20 hours for each orientation of the magnetic field versus scattering plane. In the first run, field was oriented along the direction x-ray source –detector. In the next runs field (and the sample which was imobile versus field) were oriented at angles $\Pi/2$, Π and $3\Pi/2$ versus orientation in the first run.

3. Results and Discussion

Table I. Diffraction, crystal and atomic data of $Tb_{2.5}Y_{0.5}Fe_5O_{12}$, obtained from the Rietveld's refinement [4-6]*.

angle (k_0, k_1), B		0	$\Pi/2$	Π	$3\Pi/2$
scale factor		$4.7 \cdot 10^{-9}$	$4.7 \cdot 10^{-9}$	$5.4 \cdot 10^{-9}$	$7.1 \cdot 10^{-8}$
total intensity of reflections		$9.3 \cdot 10^5$	$9.4 \cdot 10^5$	$9.9 \cdot 10^5$	$4.6 \cdot 10^6$
total intensity of refl. (420)		$2.4 \cdot 10^3$	$4.6 \cdot 10^3$	$3.5 \cdot 10^3$	$2.6 \cdot 10^4$
total background		$1.0 \cdot 10^6$	$1.0 \cdot 10^6$	$1.1 \cdot 10^6$	$4.4 \cdot 10^6$
a [Å]		12.4264(13)	12.4227(9)	12.4185(9)	12.4379(4)
fract.	x	-0.018(4)	-0.038(3)	-0.037(3)	-0.0304(6)
coordinates	y	0.055(4)	0.057(4)	0.057(3)	0.0567(8)
of O^{2-}	z	0.153(4)	0.155(4)	0.157(3)	0.1522(8)

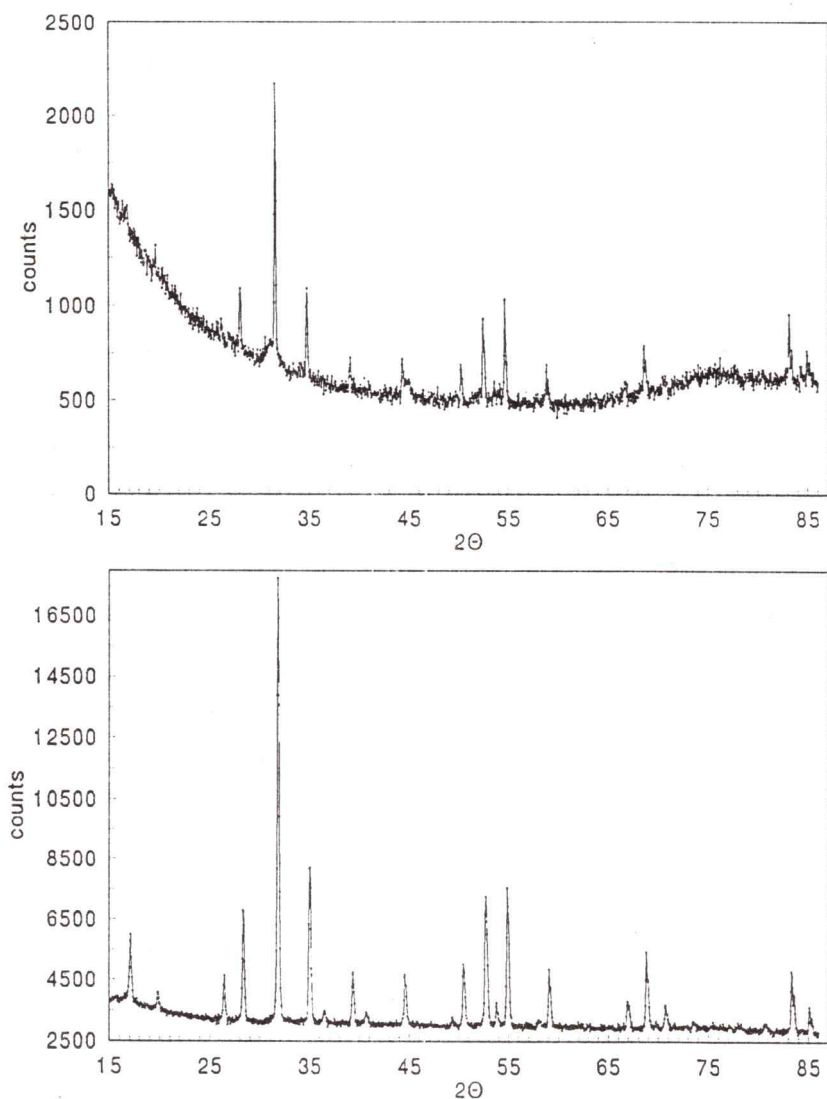*The R, Rp and Rwp factors were in the intervals 0.009-0.04, 0.02-0.04, 0.02-0.06, respectively.

Fig. 1. X-ray diffraction patterns of $Tb_{2.5}Y_{0.5}Fe_5O_{12}$ in the fields a) $\Pi/2$ and b) $3\Pi/2$ (see text).

Main differences between the data obtained in the different field orientations are shown in Table I. All Rietveld's refinements were done by using 122 reflections and 20 varied parameters.

The most interesting effect is the enhancement of diffraction for an order of magnitude at the field orientation "$3\Pi/2$". The magnetic field of the certain orientation enlarges diffraction! For a possible explanation of this phenomenon, bearing in mind that magnetic field orients domains, we note that the polycristalline sample in favorable orientation of the magnetic field becomes close to a single crystal or a perfect crystal. The nature of the entire observed effect seems to be complex because x-ray produce free electrons which move in magnetic field producing also additional electric field. This can lead to the decrease of recombination of free electrons with ions. Thus, occurred structure missis electrons and it is ordered in the magnetic field. The existence of electric and magnetic field affect the crystal structure parameters.

From the lattice constant differences the strong forced volume magnetostriction [7] with order of 10^{-4} is deduced . The above differences together with the intensity differences speak in favour of the lowering of symmetry, what is an expectable effect.

4. Conclusion

The differences of intensities and lattice constants, which depend on the magnetic field orientation versus scattering plane, point to the vector's nature of the structure amplitude in this experiment. These differences correspond to the lowering of symmetry, which is a consequence of magnetostriction and a complex behaviour of the sample under the influence of x-rays, magnetic and induced electric field.

References

1. E. F. Bertaut, IEEE Trans. Magn., 17(1981)2520.

2. R. Hock, H. Fuess, T. Vogt, M. Bonnet, J. Sol. St. Chem. 84 (1990) 39.

3. W. P. Wolf, G. P. Rodrigue, J. Appl. Phys. 29(1958)105.

4. D. B. Wiles, R. A. Young, J. Appl. Cryst 14 (1981) 149

5. C. J. Howard, R. J. Hill, AAEC Report No. M112 (1986)

6. C. L. Lengauer Rep. Germ. Min. Soc (1991) 1.

7. D. Rodic, M. Mitric, B. Prelesnik, Workshop on Magnetic Structures and Phase Transitions, Abstracts 47, Krakow, 1994.

Transport Characteristics of the Polymerized Concretes

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We analyze the transport coefficients of mass - heterogeneous structure. One typical example is the polymerized concrete. It is known that such heterogenous mixtures do not posses translationally invariant structure. For this reason they can not be analyzed by the application of the theoretical methods common to the crystals. We shall study here the diffusion coefficient of the polymerized concrete as the fundamental transport parameter. Once it is determined one can use well known expressions to relate it to the coefficient of thermal conductivity.

The theoretical analysis of the transport coefficients of polymerized concrete as an example of heterogeneous structures was performed by the combination of various approaches. We have first performed the microtheoretical analysis by the Green's function methods which lead to the analytical form of the diffusion coefficient of the phonon gas in the concrete. Since the concrete is built of inequal molecules, the diffusion coefficient will depend on the distribution of molecular masses. In order to obtain the final expression for the diffusion coefficient, it is necessary to perform the second part of the analysis, i.e. to average the microtheoretical expression over the dynamical probability for the mass distribution:

$$W(y) = \frac{T_c}{T} y e^{-y\sqrt{T/T_c}} \; ; \quad u \in [0, \infty]$$

Here $T_c = \theta_c/k_B$ where θ_c is the monomer bond energy in the crystal.

The analysis performed has shown that both diffusion coefficient and thermal conductivity coefficient of the heterogeneous structure decrease with the temperature increase. Diffusion coefficient follows $T^{-1/2}$ law :

$$D(T) = \frac{Nh}{2\mu} \sqrt{\frac{T_c}{T}}$$

where μ is the total mass of the structure and N is the total number of the molecules. Thermal conductivyt coefficient decreases much faster, i.e.:

$$\lambda \sim T^{-3/2}$$

Since above results agree well with the empirical data, one can say that the proposed method can have broader application in the theoretical study of physical properties of mass - heterogenous structures.

SUBSTITUTION OF SODIUM IONS BY COPPER(II) IONS IN HYDRATED ZEOLITE A

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Physico-chemical properties of a given type of zeolite depend to a large extent on the type of counterions present in the microporous aluminosilicate framework. This is especially true when the ions are those of transition metals.

In view of the use of zeolites as catalysts, it has been known that the copper(II)-substituted zeolites exhibit very good catalytic activity (oxidation of CO and propylene, cyclodimerization of butadiene, etc.). In that context the possibilities of exchanging sodium ions by copper(II) ions in zeolite A ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.5H_2O$) has been examined. Namely, according to our knowledge it has not been possible so far to accomplish that particular ion exchange in a 100% degree since a destruction of the sodalite crystal lattice occurred.

In a series of experiments carried out in very dilute solutions of copper(II) sulphate we have succeeded, by varying the $m(A)/V(CuSO_4)$ ratio, in achieving different cation exchange degrees (10-100%) in zeolite A, while avoiding the destruction of the sodalite lattice. Typical powder diffractograms of the obtained products are shown in Fig. 1.

In view of the different exchange degrees achieved, the water content and the unit cell parameter of the products have been determined. It is seen that the increase of the exchange degree is accompanied by an increase of the zeolite A water content (this being a consequence of exchanging a larger by a smaller ion), while the cell parameter decreases.
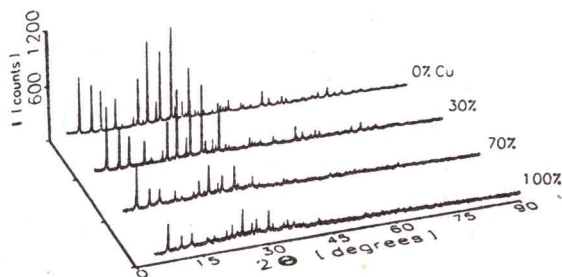
Copper(II)-exchanged Zeolite A

Figure 1. Powder diffractograms of some Cu-exchanged zeolite A samples.

Slika 1. Rendgenski dijagrami praha nekih Cu-supstituisanih zeolita A.

On the basis of the intensity change of the diffraction lines it is possible to make an assumption regarding the position of the Cu(II) ions in the sodalite lattice: Cu(II) ions are partly located in the centers of β-cavities.

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CHARACTERIZATION OF THE QUASIQATERNARY AgTlSbBiS$_4$ PHASE FROM THE Ag$_2$S-Tl$_2$S-Sb$_2$S$_3$-Bi$_2$S$_3$ SYSTEM

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A B S T R A C T : The experimental synthesis of the complex geological systems such as Ag$_2$S-Tl$_2$S-Sb$_2$S$_3$-Bi$_2$S$_3$ provides us with valuable information on the phase relations existing in such complex and heterogeneous systems under defined physicochemical conditions. The dry laboratory synthesis was performed in quartz ampoules on 200°C, due to the fact that this temperature is the most similar to the natural conditions. The most of the minerals, belonging to this system, in the nature appear under the same conditions. All phases, with in advance known stochiometry, experimentally obtained, were investigated with light microscope and by X-ray diffraction in purpose to determine its homogeneity and crustal state. This procedure revealed a completely new phase AgTlSbBiS$_4$ (Grzetic & Moh, 1991, Moh & Grzetic, 1993). This new phase is stable in the presence of the following minerals: matildite (AgBiS$_2$), miargyrite (AgSbS$_2$), weissbergite (TlSbS$_2$) and pyrargyrite (Ag$_3$SbS$_3$), qasibinary phases: TlBiS$_2$ and SbBiS$_3$, as well as with qasiternary phases: Ag$_3$Tl$_3$Sb$_2$S$_6$ and Ag$_4$Sb$_3$BiS$_8$.

X-ray powder diffraction analysis of the AgTlSbBiS$_4$ phase was performed by use of Guinier camera and by X-ray powder diffractometer procedure with Cu Kα monochromatic radiation. The powder diffraction patern of AgTlSbBiS$_4$ is very similar to that of galena (PbS), but is showing lower simmetry. Applying standard crystallografic procedure all diffraction lines were indexed on a monoclinic cell with a = 12.750(4) Å, b = 4.415(4) Å, c = 13.174(5) Å, β = 97.51(3)$^\circ$, V = 735.3(6) Å^3. This cell is similar to the cell of miargyrite (AgSbS$_2$). Systematic absences indicated that the space group is not A2/a but P2, Pm or P2/m.

Grzetic & Moh, (1991), Euro.Jour.Miner.Vol.3, Beiheft 1, 105.
Moh & Grzetic, (1993), Chem.Erde, Vol.53, 273-288.