

THE SWEDISH RESEARCH COUNCILS' LABORATORY

Studsvik, Fack
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Research report

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PROGRESS REPORT 1975

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- LF-62 Progress report 1974.
- LF-63 The spin distribution of spallation products. Yields of isomeric states. By G. Rudstam.
- LF-64 Energy spectra of delayed neutrons from separated fission products. Part IV. The precursors ⁸⁸Br, ⁹⁰Br, ¹³⁸I, ¹⁴⁰I, ¹⁴²(Xe + Cs) and ¹⁴⁴Cs. By S Shalev and G Rudstam.
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*The Swedish Research Councils' Laboratory
Progress Report for 1975
Editor: Gösta Rudstam*

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INTRODUCTION

The Swedish Research Councils' Laboratory herewith presents its progress report for 1975. The report summarizes the current projects carried out by the research groups working at the laboratory.

The very efficient assistance of the staff of the laboratory is gratefully acknowledged.

The laboratory has been financially supported by the Atomic Research Council, the Medical Research Council, the Natural Science Research Council, and the Board of Technical Development. Valuable support in various ways has also been given by the Atomic Energy Company (AB Atomenergi).

Gösta Rudstam

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The Swedish Research Councils' Laboratory

Nuclear Structure Group

(Professor N Ryde and N Olsson, Chalmers University of Technology, Gothenburg)

The facility for extracting monoenergetic neutron beams from the R2 reactor, described in earlier progress reports, has been transferred to a radial beam hole of the reactor. Measurements have been performed on the iron filter producing a beam of 24 keV neutrons with a half width of about 1 keV. The neutron flux is 10^6 neutrons/cm²sec. The flux of thermal neutrons is less than $6 \cdot 10^2$ neutrons/cm²sec. The gamma background is less than 320 mrem/h. 90 % of the neutrons in the beam fall within the energy region 24.5 ± 2.5 keV. In a program for development of detectors AB Atomenergi has started measurements on different kinds of detectors. In cooperation with professor L Ehrenberg, Wallenberg Laboratory, Stockholm, and dr R Bergman, AB Atomenergi, the genetic changes produced by monoenergetic neutrons in the intermediate energy region, will be studied. The first investigation covers studies of mutation and chromosome aberrations induced in grains of barley (Hordeum) by irradiation with 24 keV neutrons.

A series of measurements of cross sections for intermediate neutrons in different materials will be started. The interest is especially centered on reactor materials for which accurate values of cross sections are not available.

It is planned to provide the facility with a 2 keV scandium and a 144 keV silicon filter.

List of publications

N Ryde, Production and use of monoenergetic neutron beams in the epithermal and intermediate energy region, Proc 1st Scient Conf of the Iraqi Atomic Energy Commission, Baghdad, April 7-12, 1975 (in press).

The Swedish Research Councils' Laboratory

Nuclear Spectroscopy Group

(B. Fogelberg, H. Tovedal)

The experimental situation at the OSIRIS mass-separator facility was greatly deteriorated when the original PDP-9 computer system was returned to the National Defence Research Institute. In particular studies of $\gamma\gamma$ -coincidences became very time consuming when only hard-wired multichannel analyzers were available. It is thus satisfying that during the year, a new computerized data collection system has been installed (ND 4420 with 32 K memory). We hope to be able to use the full potential of this system from the beginning of 1976, and a number of complementary experiments connected to current investigations, which are unnecessarily time consuming to perform using the hard-wired systems, have therefore been postponed until 1976. The experimental activity during the present year has mostly consisted in measurements of life times of excited states and measurements of singles γ -ray and electron spectra. The current research projects will be briefly discussed below.

Finally, one should mention that a new fast tape transport system for sources have been connected between OSIRIS and the double focussing β -spectrometer. A fair amount of work with the electronic equipment is still necessary before this spectrometer is operable.

Studies of the odd-mass isotopes of Cd

The work on the decays of $^{117,119}\text{Ag}$ to $^{117,119}\text{Cd}$ is now essentially completed. A report on the study of ^{119}Cd have been published and another report on the study of ^{117}Cd has been prepared. In both nuclei low-lying $7/2^-$ and $9/2^-$ levels were observed, which can probably be interpreted as "dressed" three quasi particle states¹⁾. Similar states, at somewhat higher excitation energies, have previously been suggested^{2,3)} also in $^{113,115}\text{Cd}$. In the analysis of our data on $^{113,115}\text{Cd}$ we have found disagreement on several points with the work of refs.^{2,3)}. We therefore plan to continue the studies of $^{113,115}\text{Cd}$, through more extensive $\gamma\gamma$ -coincidence measurements and additional measurements of level half-lives.

Studies of the odd-mass Sn isotopes with $A = 119-125$

(This work has been performed in collaboration with K. Fransson, M. af Ugglas and L.-E. de Geer from the Research Institute for Atomic Physics in Stockholm).

The spin-flip decays of the $g_{9/2}$ ground states of the odd-mass In isotopes to the $g_{7/2}$ levels in isotopes of Sn provide a very suitable means to strongly populate these $g_{7/2}$ levels. The subsequent de-excitation of the $g_{7/2}$ levels can easily be studied at the OSIRIS facility where strong and clean sources of the In isotopes are obtained. In the present study, γ -ray and electron spectra have been recorded for $^{119,121,123,125}\text{Sn}$. The conversion coefficients were determined for several transitions in these nuclei. The half-lives of the $g_{7/2}$ levels in $^{119,121}\text{Sn}$ were also measured. Apart from the fairly well known one quasi-particle states also a number of three-quasi particle levels were found in $^{121-125}\text{Sn}$. Of special interest are the very low-lying $7/2^-$ and $9/2^-$ levels observed in these isotopes. The excitation energy of the $9/2^-$ levels, found in this study (see fig. 1), are only about half as high as is predicted by the theory¹⁾ of the "dressed" three quasi-particle excitations. We also observed a very small value for the $B(E2; g_{7/2} \rightarrow d_{3/2})$ in ^{121}Sn which can be explained as due to pairing effects. A report has been prepared.

Studies of the isobaric chains $A = 144, 145$

(Work performed in collaboration with E. Monnard, CEN, Grenoble)

The properties of heavy isotopes of Ba, La and Ce in this transitional region between spherical and deformed nuclei is of considerable interest. The present study of these nuclei, which was also mentioned in last years Progress Report, has been complemented by measurements of level half-lives. No complete analysis of the data has been made so far. As an example of the life-time measurements we show in fig. 2 a delayed coincidence curve which gives the half-life of the first 2^+ level in ^{144}Ba . The derived enhancement factor of about 40 for the E2 transition to the ground state is clearly intermediate between the values of 15-20 found for spherical nuclei in this mass region and the values of $\sim 10^2$ which are typical for deformed nuclei.

The 5.3 isomer of ^{96}Y

The decay of the 5.3 s isomer of ^{96}Y is similar to that of the 64 h isomer of ^{90}Y , in the way that no γ -rays follow the decay. The only discrete radiation following the decay consists of conversion electrons from an E0 transition from the 1594 keV 0^+ level in ^{96}Zr . The decay properties of this isomer have been studied both at OSIRIS and at the JOSEPH facility of Jülich. A report on the decay properties of both isomers of ^{96}Y has been made as collaboration between the groups at LOHENGRIN, JOSEPH and OSIRIS. It should be pointed out that the work at OSIRIS forms a rather minor part of this work.

The β -decay Q-value of ^{128}Sn

The γ -decay of ^{128}Sn proceeds to relatively high lying levels in ^{128}Sb . The end point energies of the β -branches are thus very low which makes possible a very accurate determination of the Q-value for this decay. A measurement of the Q-value has been made using high-resolution Si(Li) and Ge(Li) detectors. The result of a preliminary analysis is $Q_{\beta} = (1289 \pm 20)$ keV.

Studies of delayed neutron emitters

The studies of the γ -decay of high lying neutron unbound states have been continued. Relatively complete evaluations have been made of the γ -ray spectra following the decays of a number of delayed neutron precursors, among them ^{87}Br and ^{137}I . The available $\gamma\gamma$ -coincidence information is still very limited and further, extensive work in this direction is planned for the near future.

In the case of ^{87}Br , the neutron separation energy of the daughter nucleus ^{87}Kr is fairly well known. A comparison of the γ -ray and neutron spectra shows that γ -decay of the unbound levels in ^{87}Kr competes strongly with neutron emission up to about 300 keV above the neutron separation energy, see fig. 3. A report on the decay $^{87}\text{Br} \rightarrow ^{87}\text{Kr}$ has been published.

A comparison of the γ -ray data with the published delayed neutron spectrum is at present not possible for the decay $^{137}\text{I} \rightarrow ^{137}\text{Xe}$, since the neutron separation energy of ^{137}Xe is not known with sufficient accuracy. An attempt to determine the separation energy using the

$^{136}\text{Xe}(n,\gamma)^{137}\text{Xe}$ reaction is therefore planned to be carried out in the beginning of 1976 at the high flux reactor in Grenoble.

In several cases, excited nuclear states are directly populated by neutron transitions from the delayed neutron emitters. Studies of this process were initiated last year. The early results were promising (see last years Progress Report) and the experimental work has been continued during 1975. The data is not yet evaluated.

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- 4) L.-E. De Geer and G.B. Holm, Annual Report 1974, Research Institute for Physics, Stockholm, Sweden.
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1. H. Tovedal and B. Fogelberg, High-energy γ -rays in ^{87}Kr following the decay of ^{87}Br , Nucl. Phys. A252 (1975) 253.
2. Y. Kawase, B. Fogelberg, J. McDonald and A. Bäcklin, States in ^{119}Cd studied in the decay of ^{119}Ag , Nucl. Phys. A241 (1975) 237.
3. B. Fogelberg, Y. Kawase, J. McDonald and A. Bäcklin, Levels in ^{117}Ag and $^{117\text{m}}\text{Ag}$ (in manuscript).
4. B. Fogelberg, K. Fransson, M. af Ugglas and L.-E. De Geer, Energy levels and transition probabilities in the heavy odd-mass isotopes of Tin (submitted to Z. Phys.).
5. G. Sadler, T.A. Kahn, K. Sistemich, J.W. Grüter, H. Lawin, W.D. Lauppe, H.A. Selic, M. Shaanan, F. Schussler, J. Blachot, E. Monnard, G. Bailleau, J.P. Bocquet, P. Pfeiffer, H. Schrader and B. Fogelberg, Studies of the β -decay of ^{96}Y and of the level scheme of ^{96}Zr , Nucl. Phys. A252 (1975) 365.

Figure captions

- Fig. 1. Energy level systematics in odd-mass heavy isotopes of Sn. In addition to the $s_{1/2}$, $d_{3/2}$, $h_{11/2}$ and $g_{7/2}$ levels are shown the $7/2^-$ and the presently observed $9/2^-$ anomalous coupling states. These latter levels are observed to follow closely the trend obtained by adding the phonon energy of the nearest lighter even isotope to the energy of the $h_{11/2}$ level, indicated by dots in the figure. A $7/2^+$ level present at about 1.05 meV in $^{123,125,127,129}\text{Sn}$ can most probably be explained as the three quasi particle state obtained by a coupling of the $d_{3/2}$ particle to a phonon of the core. Information on the levels in ^{127}Sn and ^{129}Sn has been taken from ref. 4).
- Fig. 2. A delayed coincidence curve between radiation feeding and deexciting the 199.8 keV level in ^{144}Ba . From an analysis of the slope of the right hand side of the distribution a half-life of (0.85 ± 0.15) ns was deduced for this level. The solid line shows a prompt comparison time spectrum.
- Fig. 3. A comparison between the present γ -ray measurements and the delayed neutron measurements of ref. 5). The delayed neutron spectrum (solid line) has been resolved into components as shown by the dashed lines. The position and area of the 84 keV-peak is based on the assumption that the background in the 50 - 100 keV region is linear and can be extrapolated from the low energy side. Vertical bars indicate the positions and intensities of the observed primary γ -rays from neutron unbound states (assuming a neutron separation energy of 5511 keV). The γ -ray branching has not been studied. A good agreement (in energy) between the two measurements is obtained for 6 lines in the spectra.

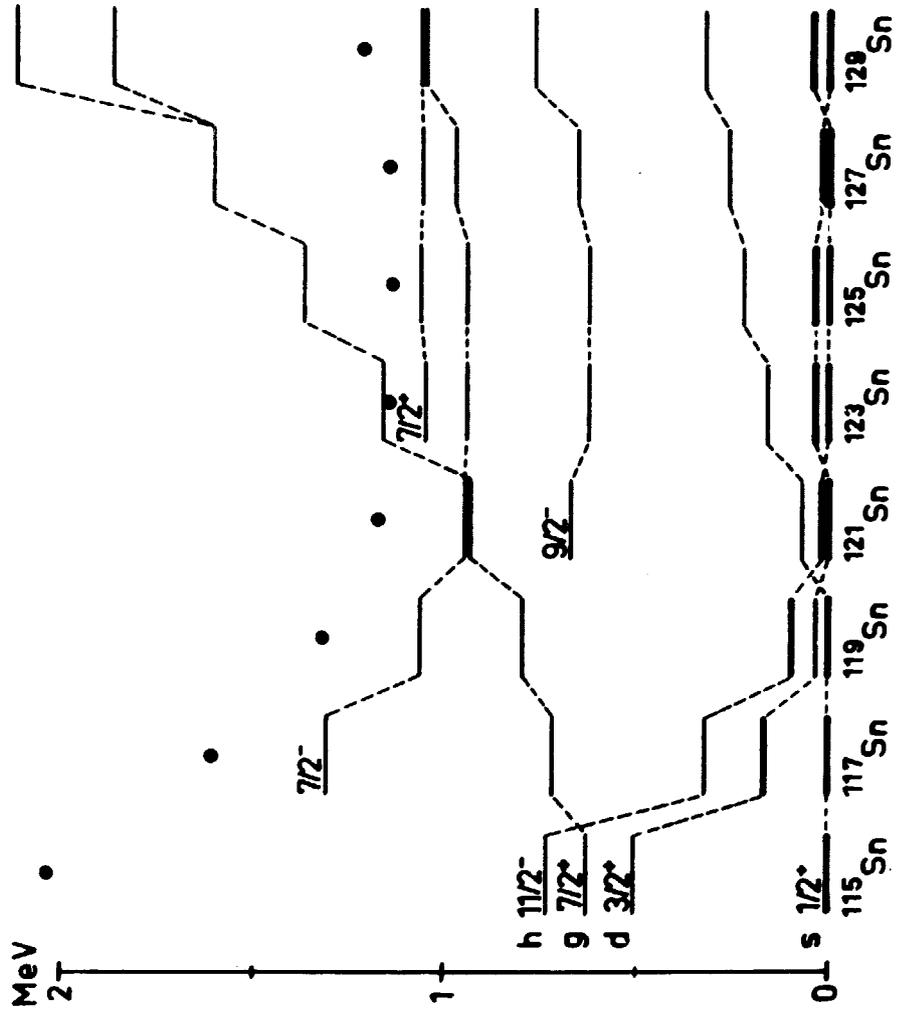


Fig. 1

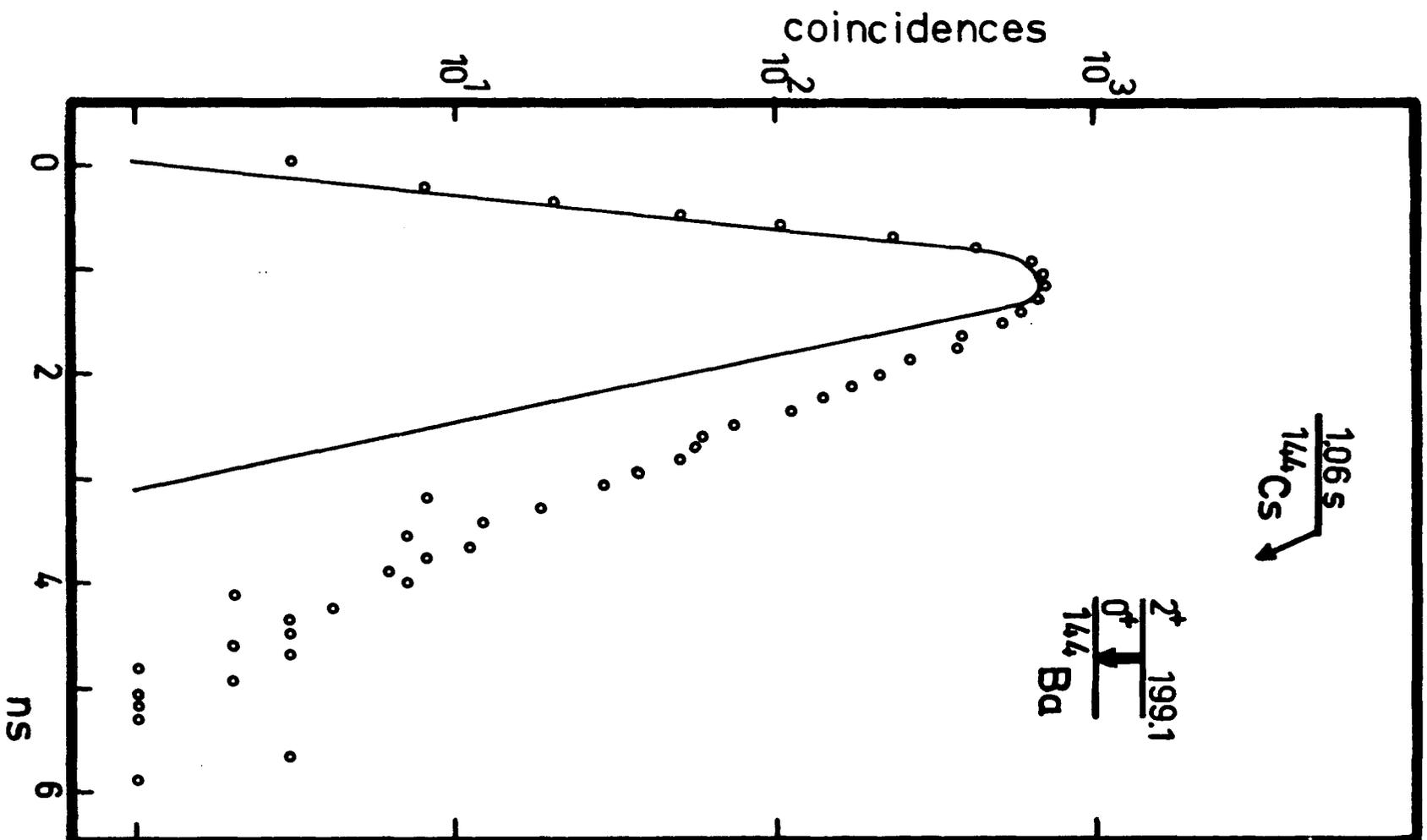


Fig. 2

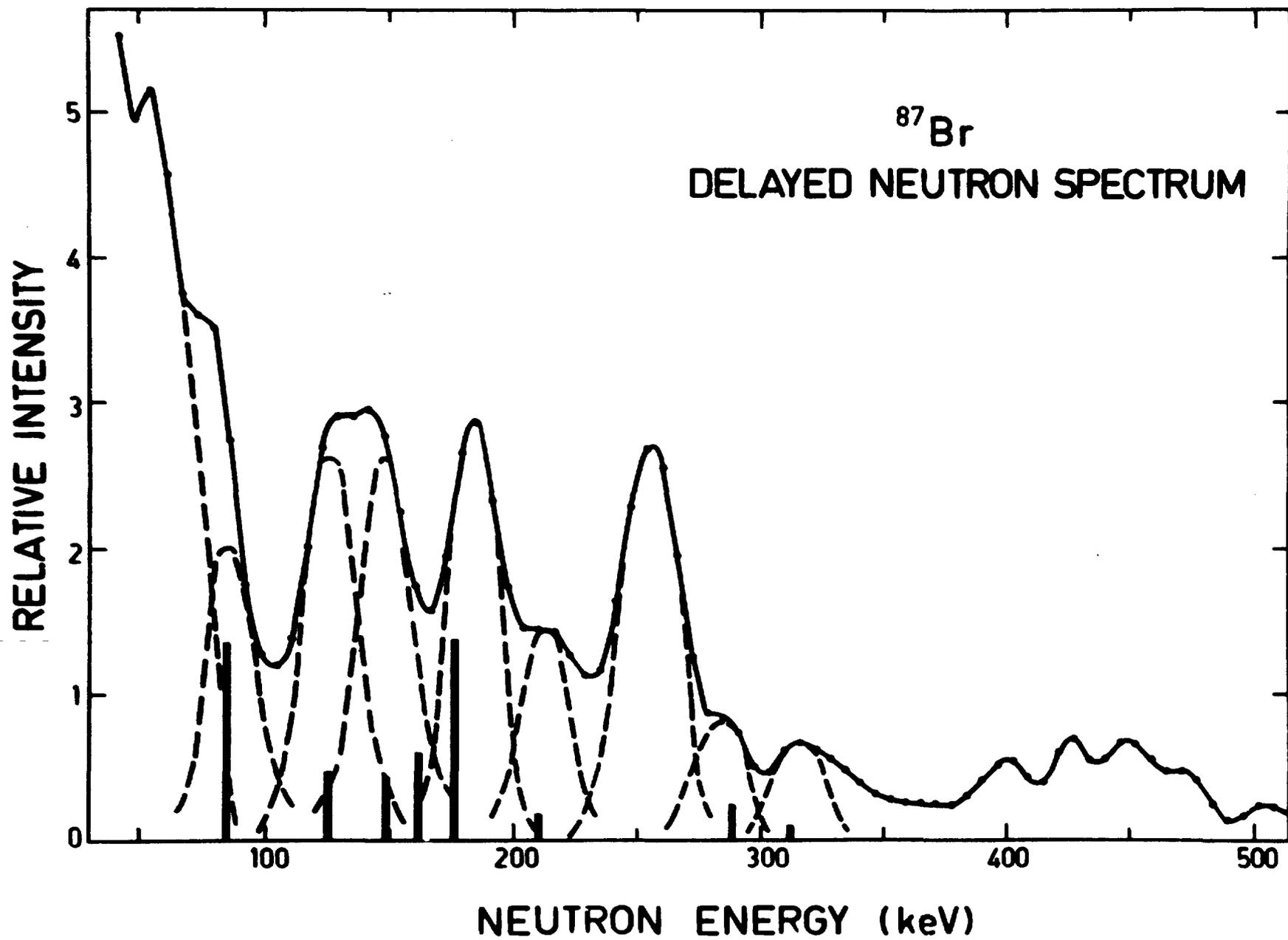


Fig. 3

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Neutron Diffraction Group

(Swedish National Committee for Crystallography)

Professor Ivar Olovsson, University of Uppsala

Neutron diffraction activities during 1975 have given fresh evidence of the high international standard both of the equipment and of the single crystal data collected. A comparison between different neutron diffraction equipments made by Dr Arne F Andresen for the Neutron Diffraction Commission has shown that the absolute flux at the specimen as determined by a gold foil measurement was 1.264×10^6 neutrons/cm².sec. This is, for instance, ≈ 3 times better than that of the comparable reactor in Petten, Holland. The measured intensity from a reflexion was even more favourable being ≈ 10 times higher.

The service activities of the group have involved cooperation with researchers from all universities in Sweden.

The well established international contacts with Brookhaven, Grenoble, Harwell and Risø have been maintained, and new valuable contacts have been made with researchers in Kjeller, Norway and Petten, Holland.

During the year a conference and a symposium on Neutron Diffraction was organized by the group at Studsvik. The interest shown both by researchers and members of the Swedish Natural Science Research Council was highly gratifying.

The year's activities can be summarized as follows:

1. Continuation of the single crystal data collection program.
2. Completion of structural investigations making use of data collected during 1974.
3. Further development of the powder diffraction equipment.
4. Full-profile refinement of powder data collected at Studsvik.
5. Conference and symposium on Neutron Diffraction.

1. The following complete three-dimensional data sets have been collected.

$\text{Na}_3 [\text{Ce}(\text{C}_4\text{H}_4\text{O}_5)_3] \cdot 9\text{H}_2\text{O}$	5 000	Inga Elding, Lund
$\text{RbH}_3(\text{SeO}_3)_2$	1 500	Roland Tellgren, Uppsala
$\text{Cs}_2\text{VOF}_4 \cdot \text{H}_2\text{O}$	1 300	Kjell Walterson, Stockholm
KHCO_3 (with cryostat)	1 200	Josh Thomas, Uppsala
$\text{Ag}_2\text{IF} \cdot \text{H}_2\text{O}$	1 600	Kenneth Persson, Lund
$\text{CsH}_3(\text{SeO}_3)_2$	5 000	Rune Liminga, Uppsala
$[\text{Co}_2\text{Cl}_2(\text{C}_2\text{H}_6\text{O}_2)_4] \text{Cl}_2$	1 900	Britt Hedman, Umeå

2. Data collected earlier have reached publication. The papers clearly demonstrate the high quality of the Studsvik data. Two abstracts are included as illustration:

A Neutron Diffraction Study of Mercury(II)chromate Hemihydrate,
 $\text{HgCrO}_4 \cdot 1/2 \text{H}_2\text{O}$

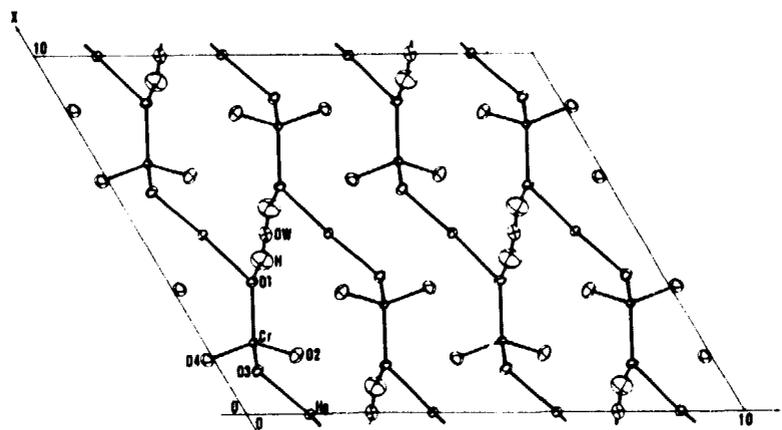
By Karin Aurivillius and Claes Stålhandske
 Chemical Center, Division of Inorganic Chemistry,
 University of Lund, S-220 07 Lund 7, Sweden.

Abstract

The crystal structure of mercury(II)chromate hemihydrate, $\text{HgCrO}_4 \cdot 1/2 \text{H}_2\text{O}$, has been refined from neutron single-crystal data (873 independent reflections) to $R = 0.030$ and $R_w = 0.023$. The crystals are monoclinic, space group $C2/c$ with $a = 11.832(1)$, $b = 5.2616(6)$, $c = 14.637(2)$ Å, $\beta = 121.01(1)^\circ$ and $Z = 8$.

The mercury atom is bonded only to two oxygen atoms, each belonging to a separate chromate tetrahedron, at the distances 2.055(2) and 2.064(2) Å, the angle O-Hg-O being $179.95(5)^\circ$. As each chromate group is bonded to two mercury atoms, fundamental building elements of the structure are endless chains of the composition $(\text{HgCrO}_4)_n$ running approximately parallel to the diagonals of the ab plane. The chains are fused by hydrogen bonds to blocks of composition $(\text{HgCrO}_4 \cdot 1/2 \text{H}_2\text{O})_n$ with thickness $c/2$ Å. There are weak interactions between the blocks, five mercury to oxygen distances varying between 2.655-2.743 Å.

In the water molecule the distances $O(\underline{W})-2\ H$ and $H-H$ are $0.945(4)$ and $1.487(6)$ Å respectively. The angle $H-O(\underline{W})-H$ is $103.7(4)^\circ$. In the hydrogen bonds the distance $(O(\underline{W})-H \cdots O)$ between water and chromate oxygen atoms is $2.961(2)$ Å with a distance $H \cdots O$ of $2.133(4)$ Å and an angle $O(\underline{W})-H \cdots O$ of $145.6(3)^\circ$.



Projection of the structure along $[010]$. The infinite chains of composition $(HgCrO_4)_n$ are running approximately parallel to the diagonals of the ab plane. The water molecules join the chains into infinite blocks $(HgCrO_4 \cdot 1/2H_2O)_n$ of thickness $\frac{1}{2}$ Å.

A Determination of the Crystal Structure of $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$ by Neutron Diffraction

(Kjell Waltersson, Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, S-104 05 Stockholm, Sweden)

The crystal structure of $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$ has been refined on the basis of three-dimensional neutron diffraction data. In an earlier study the structure of this particular compound was refined from three-dimensional X-ray diffractometer data (MoK α radiation), but the compound was erroneously given the formula Cs_2VF_6 in two earlier papers (Carpy & Waltersson, 1972; Waltersson, Wilhelmi, Carpy & Galy, 1974).

The structure is, according to the neutron diffraction study, orthorhombic, $a = 15.251(2)$, $b = 6.486(1)$, $c = 7.010(1)$ Å, $Z = 4$. $V = 693.46$ Å³; space group $\text{Cc}2m$ (No. 40). The final R_w was 0.029 for 427 independent reflexions with $\sigma(I_n)/I_n \leq 0.60$.

The structure contains strongly deformed octahedral complex ions $[\text{VOF}_4(\text{H}_2\text{O})]^{2-}$, held together by hydrogen bonds O-H---F (forming chains in the c direction) and cesium atoms inserted between them.

The vanadyl ion VO^{2+} (V-O bond distance 1.621(3) Å) is coordinated to four fluorine ligands and one H_2O molecule in trans position to the vanadyl oxygen. The V-F and the V-O distances are $2 \times 1.918(3)$ Å, $2 \times 1.924(3)$ Å and 2.290(3) Å, respectively. The O-H distance is 0.955(5) Å and the H-O-H angle $110.0(2)^\circ$.

The coordinations of the two crystallographically independent cesium atoms are quite different. Both Cs(1) and Cs(2) have eight fluorine neighbours; the Cs-F separations are in the range 3.00-3.39 Å. The Cs(1) atom is in contact with four different vanadyl oxygens at distances in the range 3.21-3.51 Å; the Cs(2) atom has only one such contact, viz. 3.28 Å. There is only one H_2O molecule within the coordination sphere of Cs(1) (3.51 Å), while Cs(2) is in contact with two H_2O molecules (3.22-3.32 Å).

3. Further development of the powder diffraction equipment.

The decision taken in 1974 to convert the old Ferranti four-circle diffractometer to function as a powder diffractometer has been completely vindicated. The necessary modifications have been completed, and there is now abundant evidence to indicate that the powder data available are of good quality (see 4). The progressive modernization of the diffractometer control system has continued to a point where automatic data collection can now be performed reliably. The earlier developed single-crystal low-temperature system has now been modified so that powder scans can also be run at reduced temperatures. An illustration of the use of this equipment for studying the para-ferromagnetic transition in Fe_2P at 214 K is given in Fig. 1.

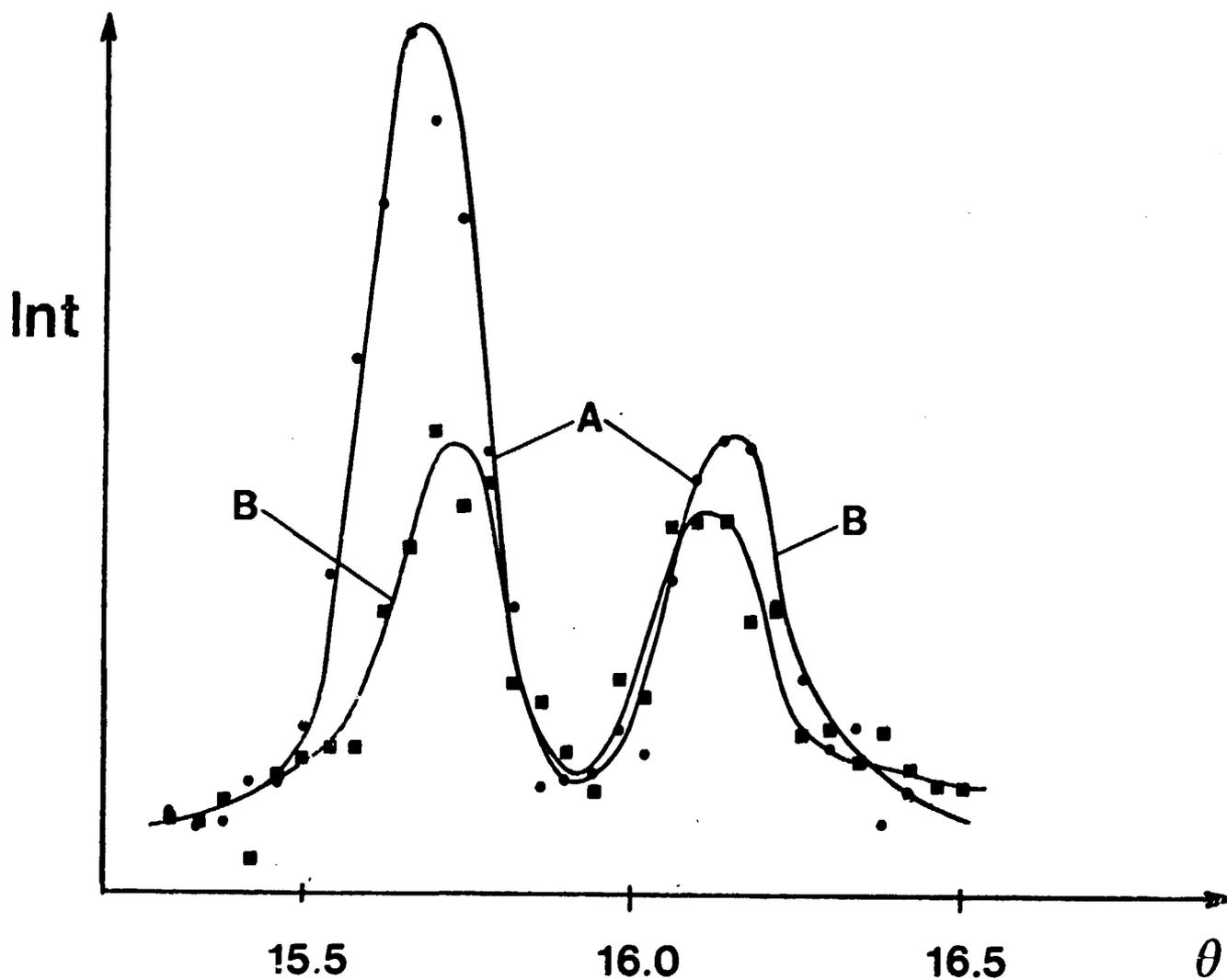


Fig. 1 A section of the neutron powder profile of Fe_2P at 160 K (A) and 298 K (B), showing the onset of the first-order para-ferromagnetic transition on cooling below 214 K.

4. Full-profile refinement of powder data collected at Studsvik

The inherent broadness of an individual line for a given reflexion (halfwidth $\approx 0.5^\circ$ in 2θ) means that, apart from in the most symmetrical of cases, account must be taken of reflexion overlap if much of the information contained in the profile is not to be lost. Such account is taken in a method programmed by Dr H M Rietveld of the Nuclear Research Center, Petten, Holland in which the intensity at any point $2\theta_i$ in the profile is taken to be given by the sum of a gaussian profile from each contributing reflexion (with centre at $2\theta_k$), i.e. $y_i = \sum_k I_k \cdot \exp[-b_k (2\theta_i - 2\theta_k)^2]$.

This assumption forms the basis of a least-squares refinement procedure in which both structural parameters and parameters describing the form of the profile are refined. The positional parameters resulting from such a profile-fitting procedure for room temperature Fe_2P are in the Table compared with the result of an earlier single-crystal X-ray diffractometer study.

Fe_2P : Hexagonal: $P\bar{6}2m$; $a = 5.867 \text{ \AA}$, $c = 3.458 \text{ \AA}$ at 298 K. $Z=3$.

	X-ray single-crystal *	Neutron powder
X: Fe(1)	0.2568(2)	0.2547(5)
X: Fe(2)	0.5946(2)	0.5951(5)
	5.6 %	4.4 %
R(F)	(258 refls.)	(34 refls.)

*) Carlsson et al. (1973) J.Solid State Chem. 8, 57.

The corresponding profile fit is illustrated in Fig. 2. It is seen that the neutron powder method is capable of producing results of comparable accuracy to those obtained from the longer and considerably more tedious single-crystal X-ray diffractometer experiment.

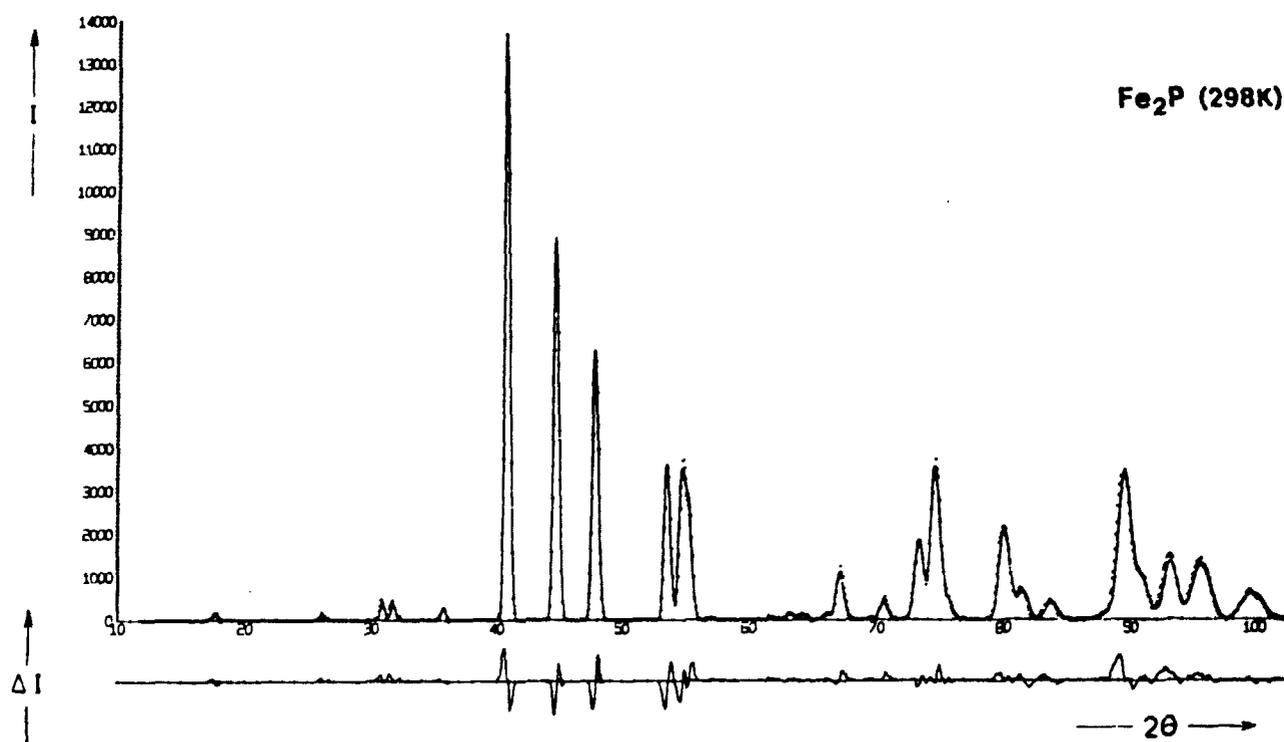


Fig. 2. An example of a full-profile least-squares fit. The dots are the observed intensities and the curve is the fitted profile. The lower curve is a plot (same scale) of the discrepancies in the fit.

5. Conference and Symposium on Neutron Diffraction

A conference and a symposium on Neutron Diffraction was held at Studsvik 13-14 November 1975. Researchers from all Swedish universities and members of the Swedish Natural Science Research Council, in all fifty persons, participated in the meeting. Representatives were also invited from neutron diffraction groups in Norway and Denmark, Dr Arne F Andresen from Kjeller and Dr Finn K Larsen from Aarhus.

The program comprised lectures, discussions, general information and a presentation of scientific papers on neutron diffraction studies made at Studsvik by the participants. A demonstration of the experimental facilities at the R2 reactor was also included.

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C Stålhandske and B Aurivillius, A neutron diffraction study of $C_6H_4(NH_3)_2Br_2$. To be published.

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The Swedish Research Councils' Laboratory

Nuclear Chemistry Group

(G Rudstam)

1. Introduction

The research activity of the group has been concentrated on the study of short-lived fission products, obtained by means of the isotope-separator-on-line facility "OSIRIS". The main effort has been connected to the determination of total decay energies. Experimental results obtained during the preceding year have been analyzed, and new determinations have been carried out with the spectrometer placed close to the collection position for an extracted beam. This means an extension of the measurements towards shorter half-lives. The possibility of measuring fission yields using OSIRIS has been investigated theoretically, and some preliminary experiments in this field have been performed.

The group is also involved in applied research aiming at an accurate determination of the decay heat effect in nuclear fuel. Methods for measuring the average beta energy per disintegration of separated fission products have been developed, and the measurements have started for light-mass products.

2. The OSIRIS facility

(B Grapengiesser, L Jacobsson, B Johansson, G Rudstam)

The isotope separator has been used regularly with a total running time of 466 hours. No major changes have been done. The new high-voltage unit delivered in 1974 has had to be returned to the manufacturer for modifications, and the old unit is still in use.

The range of elements processed by OSIRIS runs from zinc ($Z=30$) to strontium ($Z=38$) and from silver ($Z=47$) to barium ($Z=56$). It would be very interesting to fill the gap from yttrium ($Z=39$) to palladium ($Z=46$). These transition elements are very slightly volatile at the ion source temperature. There is a possibility to convert some of them to more volatile chlorides or fluorides, however, by means of hot-atom reactions in target materials such as uranium tetrafluoride or uranium tetrachloride. A crucial point is the release time to be expected from such a target material. In order to study this, a chemical separation apparatus is being constructed (see also Section 3). This

apparatus will be used for measuring the release rate of halides of elements such as tin, antimony, and tellurium. With these compounds as models it will then be possible to decide whether it is worth while to construct a target-ion source system for uranium tetrafluoride (or tetrachloride).

3. Chemical separation techniques

(B Grapengiesser, B Johansson, G Rudstam)

The separation apparatus described in the Progress Report of 1974 had excellent prestanda as demonstrated by the fact that cadmium isotopes with half-life of the order of one second could be measured after mass separation and chemical separation. Still, it must be considered as a prototype. A new version is under construction. An important improvement is the possibility to keep the collector at a well-defined temperature. This is needed for the determination of the release rates of halides from a uranium tetrafluoride or tetrachloride grain as discussed above. Similar measurements will also be performed for other target materials such as uranium oxide or carbide and for graphite. These measurements are necessary for the fission yield programme. (Section 4). In addition, it will be extensively used as a means to determine uniquely the identity of isobars in complicated cases. Such cases occur, for instance, in the mass range 125 - 130 where each mass number may contain several indium isomers in addition to cadmium and tin isotopes.

4. Delay between production and measurement in the OSIRIS system

(B Johansson, G Rudstam)

The determination of independent fission yields has been on the research programme of the group for a long time, but until now only preliminary experiments have been carried out. The main difficulty in this experiment is to correct properly for the radioactive decay in the delay between the production of a nuclide in the target material and its collection in front of the measuring apparatus. In order to find out how to make such a correction a theoretical investigation has been performed¹⁾. In this study one starts out from a general delay function and calculates the appropriate corrections to be applied. Next, the specific delay function to be expected for the OSIRIS-type arrangement is derived. If the delay is controlled by the release rate from the target surface the delay function takes the simple form

$$p(t)dt = \text{const} \times (1 - e^{-\nu t})e^{-\mu t} dt,$$

where $p(t)dt$ is the probability that the release is between t and $t+dt$, and ν and μ are parameters governing the delay. The parameter ν is determined by the dimensions of the discharge chamber of the ion source, and the parameter μ is connected to the release rate. In the case of diffusion-controlled release the delay function is composed of a series of terms, each of the form given above. All these terms have parameters connected to each other, and it is sufficient to determine one set of ν, μ -values.

In order to test the theoretical formulae a number of experiments have been carried out in which consecutive samples were measured of a particular nuclide after scrambling the reactor (*i.e.* stopping it as quickly as possible). The intensity of the samples was recorded as a function of time after the scram. This experiment was carried out with three different bromine isotopes: 32 min ^{84}Br , 3 min ^{85}Br and 55 s ^{86}Br . The results of all the measurements could be explained using the value 0.00385 min^{-1} of the parameter μ and assuming diffusion through the target material to be the time-controlling process. Although these results must be verified by other experiments also, notably experiments with the chemical separation apparatus referred to in Section 3, they indicate that it will be possible to carry out appropriate delay corrections.

Another requirement for successful fission yield studies is that the isotope separator is stable enough. This has been tested by repeated collections and measurements of the series of bromine isotopes with mass numbers 86, 87, and 88. The analysis demonstrated that the sample intensities were reproducible with a standard deviation of about 10 %. This result was obtained during a run when the separator was rather unstable owing to vacuum problems, and there is reason to expect that more accurate determinations can be carried out under better conditions. Thus, also from this point of view it seems possible to carry out a relevant fission yield programme.

5. Total decay energies of fission products

(K Aleklett, E Lund, G Rudstam)

A large part of the efforts of the group is devoted to the study of total disintegration energies for the purpose of mapping the nuclear mass surface far out on the neutron-rich side of stability. The method used for measuring nuclides of half-life longer than about 5 s is

described in detail in a manuscript which will soon be ready for publication. Using this method a large number of nuclides have been measured as reported in earlier Progress Reports. The analyses are now completed for the nuclides ^{129}Sn , ^{130}Sn , ^{130}Sb , ^{131}Sn , ^{132}Sn , ^{134}Sb , ^{135}I , ^{136}I , ^{140}Cs , and ^{143}Cs and manuscripts giving the results are being prepared.

The spectrometer for measuring decay energies has now been rebuilt and moved close to the collection position of an extracted beam. In the new position the transport time is reduced from about 3 s to less than 1 s, which facilitates the study of very short-lived nuclides. The new spectrometer has been used for measuring a number of fission products, namely $^{76-78}\text{Zn}$, $^{76-81}\text{Ga}$, $^{79,81}\text{Ge}$, ^{83}As , ^{88}Br , $^{126-129}\text{In}$, and ^{139}I , but the analysis of the results remains to be done.

Total disintegration energies for isotopes of rubidium, cesium, francium and radium have been measured using the ISOLDE equipment at CERN by a group with participation from Studsvik (K Aleklett). The results have been published in Z. Physik²⁾.

6. Delayed-neutron precursors

(E Lund, G Rudstam)

A survey of delayed-neutron precursors among the fission products was reported in the Progress Report of 1974. The results have now been written up for publication and two manuscripts, one covering the mass range 79 - 98 and the other the mass range 122 - 146, have been accepted by Phys. Rev.^{3,4)}.

Two cases have been re-examined because of discrepancies with other determinations. One is ^{140}I for which our half-life value 0.59 ± 0.01 s is at variance with the value 0.89 ± 0.12 s found by Kratz and Herrmann⁵⁾. The redetermination gave as result 0.61 ± 0.01 s, in agreement with our old value, and we conclude that this value is the more reliable one.

The other case re-examined is mass number 128 where both delayed-neutron counting and beta counting at this laboratory have yielded two short-lived activities. There is agreement only for the shorter half-life, however. For the longer one beta-counting gave a half-life of 5.6 s and neutron counting 11 s. A new series of measurements did not solve the problem. Two neutron activities always appear, the short-lived one in agreement with earlier measurements and the long-lived one with a half-life about 16 s but with poor reproducibility. In order to settle

the problem other measurements, for instance gamma spectroscopy and neutron counting after rapid chemical separation, seem necessary.

7. Delayed-neutron energy spectra

(E Lund, G Rudstam, S Shalev)

In addition to earlier published results (cf. Progress Report 1974) the analyses have been completed for another set of delayed-neutron precursors, this time with even mass numbers. The series consists of ^{88}Br , ^{90}Br , ^{138}I , ^{140}I , $^{142}(\text{Xe}+\text{Cs})$, and ^{144}Cs . The results are collected in a LF-report⁶⁾. Two new cases have been measured, namely ^{94}Rb and ^{95}Rb , but the analyses are not yet finished. This completes the study of delayed-neutron spectra for the time being, as the intensity of the remaining cases seem to be too low for spectroscopy with the present target-ion source system.

8. Determination of the decay heat in nuclear fuel

(K Aleklett, G Rudstam)

For an evaluation, by the microscopic approach, of the decay heat dissipated in nuclear fuel it is necessary to know the fission yield and the decay data for the various fission products. The decay data needed are half-lives, average beta and gamma energies, and neutron branching ratios and energies. The half-lives are already quite well known, to a large extent from work at OSIRIS. The fission yields and the neutron energies are discussed above. The neutron branching ratios will be measured in the coming one or two years. During 1975 the effort has been concentrated on the measurement of average beta energies. In these measurements a new mini-computer, acquired by the group in the Spring of 1975, has proved to be an invaluable tool. A series of programmes has been written covering the whole experimental procedure from measurement to final analysis. The measurements are carried out by repeated beta spectroscopy (by means of a Si(Li)-spectrometer) of a sample of a given mass number. Gamma spectra are then measured with a Ge(Li)-spectrometer using the same time cycle as for the beta measurements. Characteristic peaks in the gamma spectra provide a measure of the isobaric composition of the samples. This information is used for decomposing the measured beta spectra into their isobaric components. Finally, these pulse spectra are converted to electron energy spectra, and the average beta energies are calculated.

The method is capable of reaching high accuracy. An example of this is the mass chain 77 for which the values 2.12 ± 0.09 MeV, 1.57 ± 0.03 MeV, and 1.53 ± 0.06 MeV have been obtained for the isobars 1.4 s Zn, 13.0 s Ga and 52.9 s Ge, respectively. (These results are not final: a check of the response function of the beta detector remains to be done). Measurements have been carried out for mass numbers 77 (isotopes of Zn, Ga, Ge), 78 (Zn, Ga, Ge), 86 (Br), 87 (Br, Kr), 88 (Br, Kr+Rb), 89 (Kr, Rb), 90 (Kr, Rb), and 91 (Kr, Rb). According to sensitivity studies this list of nuclides contains several of those with the largest contribution to the decay heat at short intervals after stopping a reactor.

9. Spallation yields of isomers

(G Rudstam)

In order to predict the cross section ratio of isomeric states of spallation products it is necessary to keep track of the spin distribution in the nuclear reaction. The first part of a spallation reaction is a nucleonic cascade inside the nucleus which leaves the remainder of the nucleus with a certain energy- and spin distribution. These can be evaluated using Monte Carlo methods. Next, the energy is dissipated in an evaporation process leading to the final spallation product. It is necessary to follow the evolution of the spin distribution in this de-excitation process. The calculation is complicated but a programme has been written which computes the spin distribution of each spallation product. As input data may be used results from Monte Carlo cascade calculations. The computer code has been tested in a few cases. The experimental results are fairly well reproduced. The code is described in detail in a LF-report⁶⁾.

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The Swedish Research Councils' Laboratory

Radiation chemistry group

(A Lund)

Experimental studies have been performed to investigate the structure and the distribution of free radicals in molecular single crystals. Equipment for irradiation at 4.2 K has been constructed and equipment for ESR measurement at 4.2 K has been bought. Efforts have been made to finish several of the projects concerned with the application of electron spin resonance spectroscopy and quantum mechanical calculations to radiation chemistry problems to permit new research activities to be started i.e. in photo synthesis, pulse radiolysis and radiation chemistry at 4.2 K.

1. n-Alkane Single Crystals

Studies of radiation effects have been extended to 4.2 K with the aim of elucidating primary distribution of radicals, clustering of radicals in damaged regions and temperature dependence of energy transfer in deuterated crystals doped with protiated molecules. The studies are almost completed and the results are presently being summarized in an article (1.1).

1.1 Deposition of radiation energy in solids as visualized by the distribution, structure and properties of alkyl radicals in γ -irradiated n-alkane single crystals.

(T Gillbro and A Lund)

This paper summarizes earlier results from ESR work on γ -irradiated n-alkane single crystals. It also contains some new experimental results that serve to give a more complete picture of the deposition of radiation energy in solid alkanes. The experiments with solid n-alkanes done so far have provided structural data so that the nature and even the conformation of alkyl radicals are well understood. Two types of radicals exist; one located next to the end methyl group; the other in the interior of the chain. The first type has a conformation which differs from the conformation of the undamaged molecule. Microwave saturation data show that there is a difference in relaxation properties, which can be understood by a difference in mobility. Relative yield

measurements give the distribution of isomeric alkyl. This distribution differs from that measured by product analysis in liquids. For protiated n-alkanes n-alkyl is lacking and the 2-alkyl concentration is higher than expected. For deuterated n-alkanes the ESR spectrum is mainly that of radicals located in the interior of the carbon chain. Again this isotope effect is contrary to observations in liquid n-alkanes.

The broad lines observed in protiated alkanes irradiated at 77 K and deuterated alkanes irradiated at 4.2 K are not believed to arise from strong spin-spin interactions but are thought to arise from distorted crystal and radical structure in the damaged regions of the crystals.

Radical pairs exist with different stability, yield and structure. Our estimate, that as much as 40 % of the radicals are formed in pairs or clusters at 4.2 K in deuterated alkanes shows that radical pair formation is an important radiolytic process in solid n-alkanes. Energy transfer from deuterated to protiated molecules has also been experimentally verified. This energy transfer is temperature dependent and occurs efficiently at 77 K, but less efficiently at 4.2 and 273 K. There also exists a relationship between the amount of radical pairs at 4 K and the long range energy transfer at 77 K in deuterated alkanes. This can be explained very well by an exciton transfer mechanism. It might also be qualitatively explained by a hydrogen abstraction process. In this case, however, the properties of the deuterium atoms are quite unexpected.

1.2 High yield of radical pairs in deuterated n-alkane single crystals γ -irradiated at 4.2 K

(T Gillbro and A Lund)

Following γ -irradiation at 4.2 K ca 40 % of the radicals in n-decane-d₂₂ crystal are paired compared to ca 3 % following irradiation at 77 K. Two structurally different kinds of radical pairs have been observed. One kind is similar to that formed on irradiation at 77 K and shows a hyperfine splitting of 2.5 G. The second kind shows no hyperfine structure and is thought to consist of two slightly differently oriented alkyl radicals that are trapped in the damaged regions of the crystal lattice. The distance between the radicals in this kind of pair is clustered around two values, namely 10.0 ± 0.5 and 7.5 ± 0.5 Å. The value of 10 Å is believed to be a good measure of the spur radius. The high

yield of radical pairs at 4.2 K as compared to 77 K is explained by a mechanism where the excess excitation energy is trapped more efficiently at the original site of deposition at 4.2 K. This will also lead to less energy transfer to the surrounding molecules at 4.2 K.

(Chem Phys Letters 34, 375 (1975))

1.3 Anisotropic γ -proton coupling and α -, β - and methyl-proton hyperfine coupling tensors in the 2-hexyl radical

(T Gillbro, A Lund and Y. Shimoyama)

The 2-hexyl radical, $\text{CH}_3\dot{\text{C}}\text{H}(\text{CH}_2)_3\text{CH}_3$, has been produced selectively by γ -irradiation in an n-hexane- d_{14} crystal containing 0.25 % n-hexane. The full coupling tensors of the α -, β - and methyl-protons have been obtained and are found to have the principal values (36.1, 20.5, 12.1), (36.1, 32.4, 32.4) and (27.6, 24.1, 23.8) G respectively. It was possible to resolve the γ -proton coupling in some directions by virtue of the narrow linewidth in the deuterated crystal and the principal values were estimated to be (2.2, -0.5, -0.5) G with an isotropic coupling of ca. +0.45 G. It is concluded that a rotation around the C_2 - C_3 bond of roughly 180° occurs when the 2-hexyl radical is formed from the parent molecule.

(Chem Phys Letters 32, 529 (1975))

2. Organic sulfides

Organic sulfides are of great interest as a protective agent in the radiation chemistry of living cells. This work was undertaken in order to explore the structure and properties of sulfurcontaining free radicals, e.g. $\cdot\text{SCH}_3$, $\text{CH}_3\text{SSCH}_3^+$ and thiopen radicals.

2.1 Structure of oxidized and reduced disulfide bonds as calculated by the CNDO/2 method

(T Gillbro)

CNDO/2 calculations show that disulfide cation radicals, e.g. HSSH^+ and $\text{CH}_3\text{SSCH}_3^+$, have a trans-planar structure in contrast to the twisted structure of the parent molecule. The main reason for this difference is the removal of an electron from the sulfur lone-pair orbitals. The bond energy in the disulfide cation radical is much lower than in the parent molecule, which makes the reaction $\text{CH}_3\text{SSCH}_3^+ \rightarrow \text{CH}_3\text{S}\cdot + \text{CH}_3\text{S}^+$ allowed, as observed previously in radiolysis of CH_3SSCH_3 single crystals.

2.2 ESR study in γ -irradiated crystals of thiophene and 2-chlorothiophene

(S Nagai and T Gillbro)

Single crystals and polycrystals of thiophene and 2-chlorothiophene were γ -irradiated at 77 K. Analyses of the ESR spectra indicates that cation radicals and hydrogen atom addition-type radicals of thiophene are formed at 77 K and the latter radicals undergo addition reaction to thiophene at temperatures higher than 193 K to form similar radicals in dimeric form. The highly anisotropic spectrum observed from 2-chlorothiophene was assigned to the anion radical of the parent molecule on the basis of spin densities calculated by the CNDO method.

3. Alkyl halides

Alkyl halide crystals have been irradiated to determine the structure of halogen containing radicals. The $\cdot\text{CHCl}_2$ radical has been experimentally investigated in single crystal CH_2Cl_2 by ESR and ELDOR techniques and theoretically by ab initio calculations and ESR line shape analysis. Attempts to determine the structure of radicals in CHCl_3 , CCl_4 , CH_3I and CH_2I_2 have as yet not been successful. One reason is the complication caused by electric quadrupole interactions with the halogen nuclei to the appearance of the ESR spectra, a problem which has been investigated by theoretical means (3.2).

3.1 EPR and ELDOR studies of $\cdot\text{CHCl}_2$ in γ -irradiated single crystal dichloromethane

(A Lund and T Gillbro, D D Feng and L Kevan)

Single crystal dichloromethane grown in quartz tubes was γ -irradiated at 77 K. By studying both CH_2Cl_2 and CD_2Cl_2 with a combination of electron paramagnetic resonance at 9 GHz and 35 GHz together with electron-electron double resonance, it is concluded that the dominant radical formed is $\cdot\text{CHCl}_2$. Thus in this matrix it appears that dissociative electron capture is not the main net reaction generated by ionizing radiation.

(Chem Phys 7, 414 (1975))

3.2 Analysis of EPR with large quadrupole interaction

(K Å Thuomas and A Lund)

A method has been developed to analyze EPR spectra for the case when the quadrupole coupling and the hyperfine coupling are of comparable magnitudes but much smaller than the electronic Zeeman term. A computer program which calculates the EPR spectrum for a finite Gaussian or Lorentzian line width has been written. The program is particularly suitable for cases with several interacting nuclei.

The method has been applied to confirm the experimentally observed planar structure of $\cdot\text{CHCl}_2$. Ab initio UHF calculations have further confirmed this structure.

Geometry optimization of $\cdot\text{CH}_2\text{Cl}$ has shown that the radical can be assumed planar at least on the ESR time scale.

(Accepted for publication in J. Magnetic Resonance).

5. Analysis of EPR and ENDOR data

A computer program has been developed to calculate ESR spectra from radicals containing one or several nuclei which give rise to magnetic hyperfine - and electric quadrupole interactions. During a visit in Paris (A L) a version of the program was developed in cooperation with J Maruani to permit calculations of powder spectra. After completed tests a technical report will be written describing usage of the program.

5.1 Evaluation of hyperfine and quadrupole tensors from ENDOR measurements on single crystals

(K Å Thuomas and A Lund)

A method has been developed for evaluating the hyperfine and quadrupole tensors A and Q from ENDOR measurements made on single crystals. The method is applicable even when the tensors do not have common principal axes.

An analysis has been made of the modifications required when the first order analysis based on the assumptions that $g\beta B \gg G, F$ and $G \gg P$ is not sufficiently accurate. The second order hyperfine energy contribution and the cross product of fine and hyperfine energy contribution of the order $FG/g\beta B$ both cancel when the two frequencies corresponding to the transitions $(M, m) \rightarrow (M, m-1)$ and $(-M, -m) \rightarrow (-M, -m+1)$ are added. P is the quadrupole coupling term.

The method has been applied to re-analyze the ^{14}N ENDOR data for NO_2 . The principal values of the ^{14}N quadrupole coupling obtained here, namely -0.2, -1.4 and 1.6 MHz, differ significantly from those obtained assuming parallel principal axes for A and Q whereas the hyperfine coupling tensor is the same in the two cases.

(J Magnetic Resonance 18 12 (1975))

6. Ab initio and semiempirical calculations

The calculations were performed with the aim of calculating magnetic hyperfine coupling constants and electric quadrupole coupling constants of free radicals. The ab initio calculations have been discontinued due to lack of manpower and lack of funds to cover costs for computer time.

- 6.1 Ab initio MO LCAO UHF calculations of magnetic hyperfine interactions in π -radicals isotropic and anisotropic couplings of $\cdot\text{CH}_3$, $\cdot\text{NH}_3^+$, C_2H_5 and $\cdot\text{N}_2\text{H}_4^+$

(J Almlöf, A Lund and K Å Thuomas)

A series of π -electron radicals have been investigated with ab initio methods, using the unrestricted Hartree-Fock approximation. The geometries have been partially optimized, and magnetic hyperfine coupling constants have been evaluated. For the dipolar hyperfine couplings, the results obtained are in fair agreement with experiment, whereas the isotropic coupling constants show greater deviations. These values are also shown to be sensitive to annihilation of the quartet contamination of the wavefunction.

(Chem Phys 7, 465 (1975)).

- 6.2 Ab initio MO LCAO UHF calculations of the stability in dimeric ethylene radical ions

(J Almlöf, A Lund and K Å Thuomas)

The stability of ethylene dimer ions has been computed by ab initio methods. The positively charged dimer is stable (0.6-0.7 eV) while the neutral and the negatively charged dimers are unstable with respect to decomposition into monomers. The magnetic hyperfine coupling constants have also been evaluated, hyperfine splittings are half those in the monomer in agreement with experimental data.

(Chem. Phys. Letters 32, 190 (1975)).

- 6.3 Theory for the anisotropic hyperfine coupling with fluorine: the $\cdot\text{CF}_3$ radical

(O Edlund, A Lund, M Shiotani, J Sohma and K Å Thuomas)

A method has been developed to estimate the anisotropic hyperfine interaction for ^{19}F in fluorinated radicals based on INDO theory. The dipolar integrals have been calculated using Slater type orbitals. Careful selection of effective nuclear charges, different from those obtained by Slater's rules, and adjustment for the valence electron distribution proved necessary in order to obtain agreement between theory

and experiment. The method has been applied to a prototype system, the $\cdot\text{CF}_3$ radical. The results confirm a pyramidal structure with a F-C-F bond angle $\theta = 109.5^\circ - 112.0^\circ$ and a C-F bond length of 1.30 - 1.35 Å. With $\theta = 111.1^\circ$ the dipolar tensor is calculated to be (122.2, -55.5, -66.7) G close to the experimental result (120.0, -56.5, -63.5) G.

An ambiguity in the determination of the sign of the angle α' between the 120.0 G component and the C_{3v} axis was found to occur experimentally but not theoretically.

According to experiment $\alpha' = \pm 17.8^\circ$ where the negative sign corresponds to an axis perpendicular to the C-F bond. INDO theory gives $\alpha' = 26.8^\circ$. Ab initio theory confirms the pyramidal structure with $\theta = 111^\circ$ and $\alpha' = 19.7^\circ$. Thus the 120 G component is believed not to be perpendicular to the C-F bond, but to make an angle of about 54° with the bond axis. This result is explained by the contribution to the dipolar couplings from spin density in ^{19}F 2p orbitals. In this instance bond directions cannot be obtained from ESR data without detailed analysis of the electronic structure.

(Submitted for publication)

6.4 Theoretical investigation of the diboranyl radical $\dot{\text{B}}_2\text{H}_5$

(Ove Edlund and Junkichi Sohma)

Based on the structure of the neutral diboranyl ($\dot{\text{B}}_2\text{H}_5$) radical, which was proposed from the analysis of ESR spectra, the dipolar coupling tensors of the boron, the bridging hydrogen and the terminal hydrogens in this radical have been calculated by means of the analytical formulae for the dipolar integrals used by Barfield and others. The calculated dipolar tensors were found to be in good agreement with the experimental results. The calculations confirm the configuration proposed by Hasegawa and Sohma for the $\dot{\text{B}}_2\text{H}_5$ radical.

(Molecular Physics, Vol 29, 4 (1975) 1229-1239).

6.5 Theoretical estimation of the hyperfine coupling tensors in the $\dot{\text{C}}_2\text{H}_5^-$ and $\dot{\text{C}}_2\text{F}_5$ radicals

(O Edlund and J Sohma)

The hyperfine coupling tensors of the hydrogen-, fluorine- and carbon nuclei in the $\dot{\text{C}}_2\text{H}_5^-$ and $\dot{\text{C}}_2\text{F}_5$ -radicals have been estimated by the INDO approximation method. The analytical formulae for the dipolar

integrals derived by M Barfield have been used in order to calculate the anisotropic part of the tensors. The tensors have been rotationally averaged about the C-C axis. The results obtained agree well with the experimental results. It is of special interest to observe that the theoretical results obtained for the rotationally averaged anisotropic part of the beta-fluorine coupling in the $\dot{\text{C}}_2\text{F}_5$ -radical support the experimental result that the anisotropy averages out nearly to zero. Depending on the complex nature of the interaction between the spin density and the atomic nuclei it is shown that only two configurations are not enough to estimate the average values. This phenomenon is discussed for the protons and the fluorines in the two radicals respectively. The isotropic couplings agree well for the protons, carbons and α -fluorines but not for the beta-fluorines. These results are similar to those obtained in earlier INDO-calculations.

(To be published)

6.6 Theoretical estimation of the hyperfine coupling tensors in trimethylenemethane $\dot{\text{C}}_4\text{H}_6$, a radical in triplet ground state

(O Edlund and H Yoshida)

In ESR powder spectrum recorded for the $\dot{\text{C}}_4\text{H}_6$ radical at 4.2 K, the Z-component (perpendicular to the radical plane) of the proton hyperfine coupling tensor has been estimated to be -9.01 G. The anisotropic part of this component is attributed by several investigators to contributions from spin density located on the central carbon atom and the carbon atom nearest to the proton in question. In a more complete calculation using the same method as in the parts 6.4, 6.5 above we have found that even the contribution from spin density located on the other carbons is of the same order as from the central carbon and can therefore not be excluded in such a calculation. The anisotropic part is estimated to be -1.58 G, which is in absolute value probably somewhat too high. Because the anisotropic value is so small the exclusion of the off-center dipolar integrals can have considerable significance. It would therefore be of importance to carry out the same calculation by the ab initio method, where all kind of dipolar integrals are included.

(To be published)

6.7 ESR spectra of monoprotonated semiquinone radicals formed during photolysis of p-benzoquinone and its methyl derivatives

(T Warashina, O Edlund and H Yoshida)

Proton hyperfine coupling constants of monoprotonated p-benzo-semiquinone, durosemiquinone, 2,6-dimethyl-p-benzosemiquinone, 2,5-dimethyl-p-benzosemiquinone and methyl-p-benzosemiquinone radicals were determined from ESR spectra during photolysis of the corresponding quinones under identical conditions, i.e., in ethanol and at about 20°C. By considering all these constants together, the ESR spectra were assigned and following results obtained: (1) the hydroxyl groups were at the oxygen atom further from the methyl substituents, (2) the coupling constant was generally -1.86 - -1.65 G for hydroxylic protons, (3) the absolute value of the coupling constant for both ring and methyl protons was in the range 0-0.7 G for ortho-positions and 4.3 - 5.2 G for meta-positions relative to the hydroxyl group, and (4) the hydroxylic proton of durosemiquinone had an exceptionally small coupling constant because of steric hindrance of the methyl groups. The temperature dependence of the coupling constants in p-benzosemiquinone revealed an asymmetry of the meta-ring protons at low temperature due to the hindrance of hydroxyl group rotation. The coupling constants for p-benzosemiquinone were calculated with the INDO method. However, the results were not satisfactory because the calculated coupling constant was too large for the ortho-protons and the asymmetry calculated for the conformation with the hydroxylic proton fixed at one of the stationary sites was too small to interpret the observations.

(Bulletin of the Chem Soc of Japan, Vol 48(2), 636-640 (1975))

6.8 ESR study on PMMA main chain scission induced by mechanical fracture

(M Sakaguchi, S Kodama, O Edlund and J Sohma)

Theoretical results on model compounds support that the doublet component of the ESR spectrum from ball-milled PMMA at 77K in vacuum is attributed to a secondary radical which is produced by a hydrogen migration to the broken site of the primary radical in the main chain scission.

(Polymer Letters, Edition 12, 609 (1974)).

8. ESR studies of inorganic radical anions

Two papers have been completed. One paper deals with the structure of the radical anions formed in lithium trihydrogen selenite by γ -irradiation of the normal and the deuterated compound. The other paper deals with molecular motion of CO_2^- radicals on a zeolite.

8.1 Electron spin resonance study of γ -irradiated single crystal and powder of $\text{LiH}_3(\text{SeO}_3)_2$ and $\text{LiD}_3(\text{SeO}_3)_2$

(O Edlund and A Lund)

Gamma-irradiated monoclinic single crystals and powders of $\text{LiH}_3(\text{SeO}_3)_2$ and $\text{LiD}_3(\text{SeO}_3)_2$ have been investigated at room temperature by ESR in both the X and the Q band. Twelve species consisting of six pairs of inequivalent radicals have all been identified as SeO_2^- -type radicals pairwise located in two different sites. The origin of the difference in the principal values of the g-tensors for the radicals is attributed to a difference between the Se-O bond lengths, which in fact gives a lower symmetry of the radicals. The generation of the radicals has been explained as a rupture of a Se-O bond, which can occur in six different ways due to the crystal structure. The orientations of the radicals in the crystal are different compared to corresponding SeO_2 groups in the host crystal, and this phenomenon presumably depends either on a reorientation of the radicals or on a radical reaction. One extra splitting of peaks originating from two of the radicals in $\text{LiH}_3(\text{SeO}_3)_2$ is absent in $\text{LiD}_3(\text{SeO}_3)_2$, thus indicating hydrogen bonding to the radicals.

(J Magnetic Resonance, in press)

8.2 ESR study on molecular motion of CO_2^- radical adsorbed on zeolite

(O Edlund, J Sohma and K Sogabe)

Molecular motion of $^{13}\text{CO}_2^-$ radical adsorbed on zeolite was quantitatively analysed from the temperature variation of the separation of hyperfine structure of ESR spectra from $^{13}\text{CO}_2^-$ radicals.

(Bulletin of the Chem Soc of Japan, Vol 47(12), 3163-3164 (1974).

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- J Almlöf, A Lund and K Å Thuomas, Ab initio MO-LCAO UHF calculations of magnetic hyperfine interactions in σ -radicals. Isotropic and anisotropic couplings of NO_2 and CO_2^- radicals, *Chem Phys Lett* 28 (1974) 179.
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- Anders Lund, Tomas Gillbro, Da-Fei Feng and Larry Kevan, EPR and ELDOR studies of CHCl_2 in γ -irradiated single crystal dichloromethane, *Chem Phys* 7 (1975) 414
- T Warashina, C Edlund and H Yoshida, ESR spectra of monoprotonated semiquinone radicals formed during photolysis of p-Benzoquinone and its methyl derivatives, *Bull Chem Soc Japan* 48 (1975) 636

O Edlund and J Sohma, Theoretical investigation of the diboranyl radical \dot{B}_2H_5 , Mol Phys 29 (1975) 1229

Tomas Gillbro and Anders Lund, High yield of radical pairs in deuterated n-alkane single crystals γ -irradiated at 4.2 K, Chem Phys Lett 34 (1975)

O Edlund and A Lund, Electron spin resonance study of γ -irradiated single crystal and powder of $LiH_3(SeO_3)_2$ and $LiD_3(SeO_3)_2$, accepted for publication in J Magn Res

K-Å Thuomas, Analysis of EPR with large quadrupole interaction, AE-504, J Magn Res

T Gillbro and A Lund, Deposition of radiation energy in solids as visualized by the distribution, structure and properties of alkyl radicals in γ -irradiated n-alkane single crystals, The Swedish Research Councils' Laboratory Research Report LF-69.

T Gillbro, Structure of oxidized disulfide bonds as calculated by the CNDO/2 method (submitted for publication).

Section for Solid State Physics
(Docent Rolf Pauli)

Neutron spectrometry in the solid state

(R Stedman)

Measurements on superconducting lead revealed no change in the energy widths of phonons within an energy interval extending to just above the gap energy for this superconductor. That is, the phonon energy width arising from interaction of a phonon with conduction electrons in the normal metal (a width which should disappear for phonons below the gap energy in the superconductor) was too small to be detected, despite exceptionally good resolution. Marked structure of the lower transverse branch in the (220) direction was observed.

Supplementary measurements on a sodium sample which had undergone the martensitic transformation at 36 K and retransformation at a higher temperature failed to reveal any consistent relation between the orientation of the few large grains comprising this sample and the orientation of the original monocrystal before the transition. The investigation of the martensitic transformation in sodium is now concluded, and a paper is being prepared.

Preliminary diffractometric measurements were made on bismuth powder to see whether sufficient resolution could be obtained for the planned measurements on this material close to the melting point. It was found that an appropriate diffraction peak could be resolved, and measurements at higher temperature will be made as soon as a suitable sample holder and furnace have been obtained. The object is to investigate the distribution of the lattice spacing as the melting point is approached.

U Karlsson and G Nilsson from the Linköping University of Technology carried out measurements on different monochromator crystals and later joined our group to begin work for the doctorate. Their measurements showed that a beryllium monochromator we had obtained was not superior to good copper crystals for high energies (near 0.1 eV), as it would have been if the quality had been sufficient. Using this beryllium monochromator and, later, a copper monochromator, measurements on phonons in gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were commenced.

The new members of our group have begun measurements on temperature shifts of phonon frequencies in RbBr. This work is being led by Doc G Raunio, Linköping.

A computer programme for fourier analysis of dispersion relations in bcc and fcc structures is under preparation. This programme is intended for use in deriving an optimum version of the energy-wavenumber characteristic of the screened pseudopotential in simple metals from the dispersion relations for phonons.

A course of twenty lectures on "The Dynamics of Atoms in Crystals" was given by R Stedman at the Royal University of Technology in Stockholm during the spring.

Theoretical studies of condensed matter

(I Waller, I Ebbsjö)

The program for molecular dynamics simulations, in which the classical equations of motions for about 500 particles are successively solved, have been extended by us to liquid metals during the year. The method has earlier been applied to one component liquids such as liquid argon, to two component systems such as mixtures of argon isotopes and of argon and krypton and also to an ionic melt (NaCl).

Our computer program has successively been extended first to two component systems and later to accept as input either analytical or numerical form of the interaction energy between the particles. Furthermore, several quantities are now evaluated during the computational process. This makes it easier to judge if the system is in thermodynamic equilibrium and also if the length of the time step used is appropriately chosen.

Our calculations for liquid metals have been stimulated by the inelastic neutron scattering experiments on liquid lead which have been done at the R2-reactor at Studsvik by prof K-E Larsson and coworkers. This group are presently planning similar experiments on liquid aluminium. Also a thorough understanding of liquid metals and the numerical evaluation of their properties made possible by molecular dynamics is of technological interest.

The first task in our calculations has been to find a suitable effective pair potential for the interaction between the ions in liquid lead and liquid aluminium. It is natural to use the formalism of pseudo-potentials which has been very successful in the calculation of the dynamics of atoms in certain metals in the solid state, e g aluminium, and also for some liquid metals e g rubidium. Lead has to be investigated further because of the more complicated electronic structure in this case.

We are using two effective potentials for aluminium. They have so far been tested by calculating the pair distribution function using the molecular dynamics computer program for each of the two pair potentials. By Fourier transforming this function, the static structure factor is obtained which may be compared with experimental data obtained from neutron- and X-ray-scattering. Note that the molecular dynamics- and the Monte Carlo method are the only reliable methods available at present to calculate the pair distribution function for a given pair potential.

The first pair potential tested was obtained from Ashcroft's pseudopotential and Geldart and Vosko screening. The calculated phonon frequencies at 80 K agree very well with the experimental results by Stedman et al. Regarding the static structure factor, which has recently been published by Stallard and Davis in Phys. Rev. A8 (1973) 368, the position of the main peak of the calculated structure factor agrees well with the experimental result but the height is about 20 % too large. The molecular dynamics calculations were done for a temperature of 1300 K.

The other potential has been calculated from data given by Dr M Finnis at Harwell at atomic volumes corresponding to 80 K, 975 K and 1300 K. This potential is based on Shaw's non-local model potential and Geldart and Taylor screening. The calculated pair distribution for this pair potential differs very little from the one calculated earlier. However, although the potentials are quite different, the repulsive parts are similar which shows that the structure factor is relatively insensitive to other parts of the potential at the densities considered.

During Ebbsjö's visit at conferences in England in April ("Interatomic forces in condensed matter" in Reading, "Harwell consultant symposium on interatomic forces" and "Computational physics of liquids and solids" in Oxford) contact was established with people working with the calculation of interatomic potentials. This has led to an exchange of information which is very useful in our calculation of model potentials.

Giving T Kinell took part in the calculations with the first potential. We discussed our results with prof N H March during his visit at Studsvik in the end of May. At Dr P Schofield's visit in the beginning of August he stressed that it may be important to know the pair distribution function for larger distances than those considered during the simulation in the computer in order to get the true height and width of the peak of the static structure factor.

In cooperation with Gerhard Müller from Basel, a method was developed to solve the Ornstein-Zernike integral equation with which it is possible to extend the pair distribution function to larger distances. In this method analytical approximations for the direct correlation function for large distances are used.

Several studies where our computer programs for lattice dynamics have been used were published during the year.

List of publications

I Ebbsjö, G Müller, Extension of the pair distribution function of a liquid by solving the Ornstein-Zernike integral equation numerically, AB Atomenergi AE-FF-140 (nov 1975).

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