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STUDIA UNIV. BABEŞ-BOLYAI, PHYSICA, XXXVII, 2, 1992

SIMULTANEOUS DETERMINATION OF U AND Th FROM ROCKS BY GAMMA SPECTROMETRY

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ABSTRACT. Using the high resolution gamma spectrometry method (GeLi) was determined the U and Th content in two rocks melange with a great concentration of these elements. As standards were used two reference materials from IAEA, Viena. Uranium was determined by using eleven characteristic gamma ray energies and for thorium ten characteristic energies are used. The obtained concentrations are: 1.272% for uranium and 0.70% for thorium with relative error of 3.2% and 3.9% respectively.

Introduction. Nuclear energy development conducted to the development and improvement methods of prospecting and exploitation of U and Th ores. The measurement possibility of gamma energy emited by these elements or their radioactive descendents offers the possibility of elaboration of a rapide method, and sufficient accuarate, for the determination of U and Th from ores and rocks. Development of this method makes possible the isotopic analyses of uranium, which is necessary in process of isotopic enrichment, in determination of burning ratio and in process of reprocessing of nuclear fuel [1-4].

The procedure and results of obtaining of a U and Th standard, which can be used in simultaneous determination of these elements in rocks and ores presented.

Experimental Method. For measurement of U and Th by gamma spectrometry was used gamma spectrometry of high resolution based

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on the detection with semiconductor detectors (GeLi), which has the advantage of elimination of unliked multiple interferences during determinations.

Measurements were done at I.F.A. Bucharest in Laboratory 8 IFIN, with a help of Canberra gamma spectroscopy chain with vertical 75 cm^3 Ge(Li) detector. It was done measurements on three samples included in Table 1.

Table 1. The basic characteristics of analysed samples.

Sample Characteristic	(a) Uranium standard(US)	(b) Thorium standard(Ths)	(c) Uranium-Thorium standard(UThS)
Chemical formule	U_3O_8	$Th(NO_3)_4*4H_2O$	ore
Mass (g)	100+0.04	100+0.04	171,67+0.05
Provenance	IAEA Vienna	IAEA Vienna	pechblend+thorium ore
Concentration (mg/g)	1.009	1.945	unknown

Uranium and thorium concentration from UThS sample will be determined by comparation with the standars (a) and (b). Gamma spectra were succesively registered in the analyser memory with the following periods: Uranium standard - 3,250s, Thorium standard - 3,000s, UThS sample - 1,500s.

Results and Discussions. Gamma spectra, resulted from the measurements, were processed principally by determination of the net area under the photo-peaks, together with energetical calibration and detection efficiency.

For those two standards, the net areas of the photo-peaks were extracted directly from multichannel analyser, which das

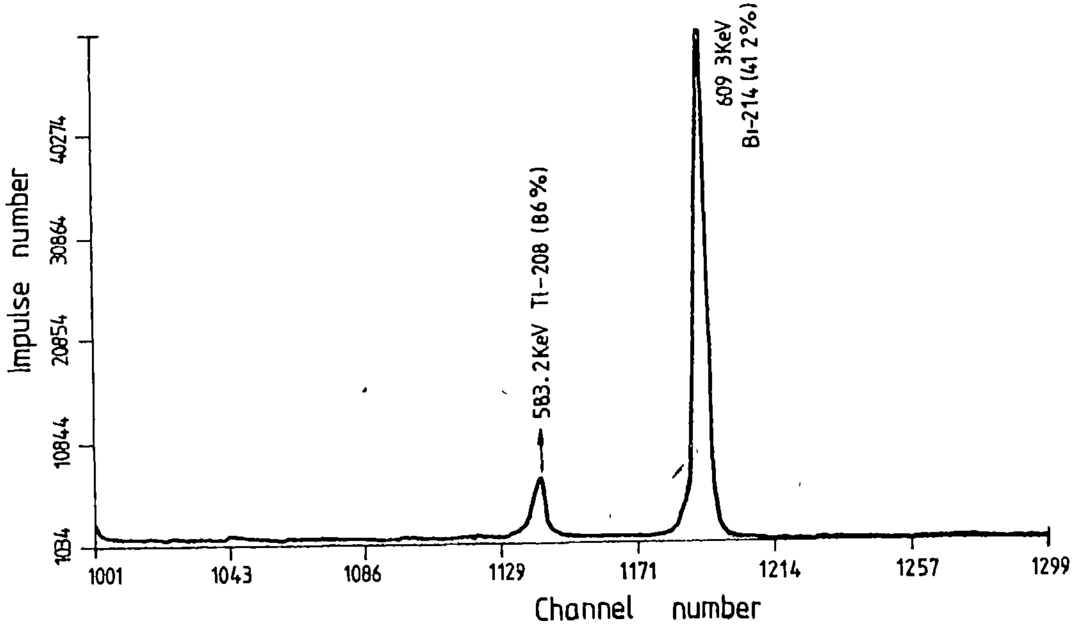

Fig.1

implemented a microprocessor for determination of these areas.

The sample spectrum being a combination of those two spectra of standards, has a high complexity. Fig. 1 - 3 present some sequences from this spectre on the limited energy interval. For this reason the spectrum was processed with the help of a SAMPO - 80 programme package introduced in a CORAL Computer of ITIM Cluj-Napoca [4]. Sample spectrum was transfered into computer, too, from magnetic tape.

The SAMPO - 80 Programme Package executes the following operations: energy calibration of the spectre, calibration in eficiency of the spectre, calibration of the peak shape, calibration of the net area.of the peaks, identification of gamma radionuclid emiters, calculation of the net activity for every

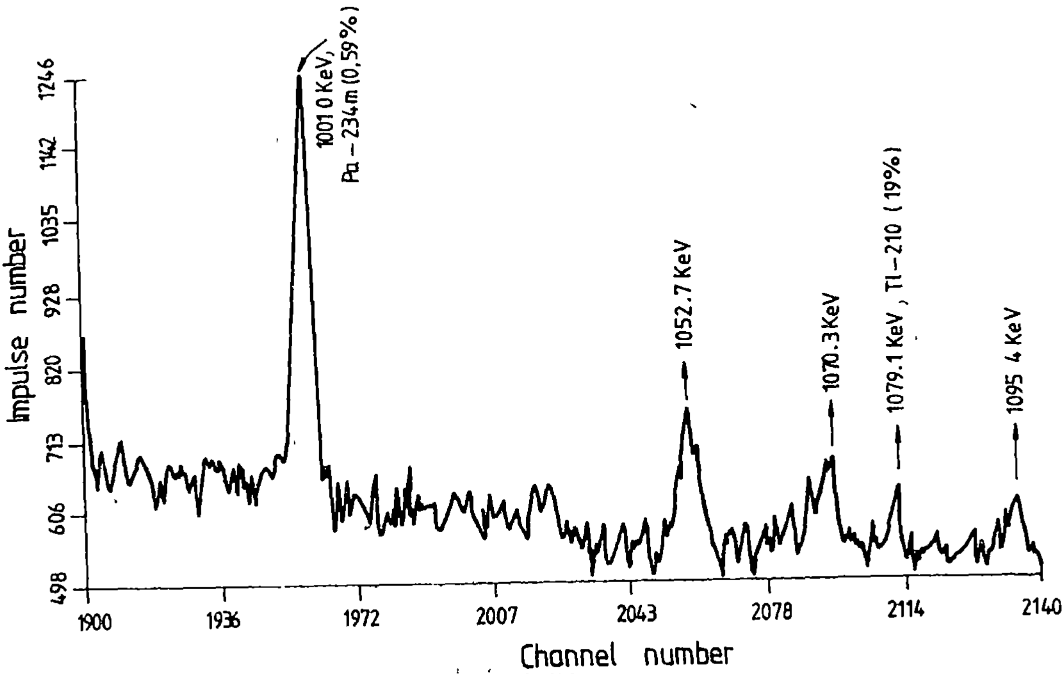

photo-peak, calculation of errors.

The heads of series of the three natural radioactive families ^{238}U, ^{232}Th, ^{235}U, emit alpha radiation and give birth at the products which at their turn are desintegrated by emission of alpha, betta and gamma radiations, untill are obtained finally stable isotopes. Actinium family (^{234}U-^{238}U) contributes to the total uranium activity with 1/138 parts.

Uranium family after half-life period, is devided in five groups:

a. ^{238}U - ^{234}U. Half-life period of ^{234}Pa of 24.1 days is much longer than of the other descendents. Radioactive equilibrum, even if it would be disturbed by some geochemical processes,is rehabilited in 5-6 months. Gamma radioactivity of this group is of 2-8%.

b. Thorium (^{230}Th) has a half-life period of 8.3 . 10^4 years and attains the equilibrium with previous group after approximately (5-8) . 10^5 years.

c. Radium (^{226}Ra) has a half-life period of 1620 years, emits alpha radiations and attains the equilibrum to ^{230}Th after 1.5 . 10^4 years.

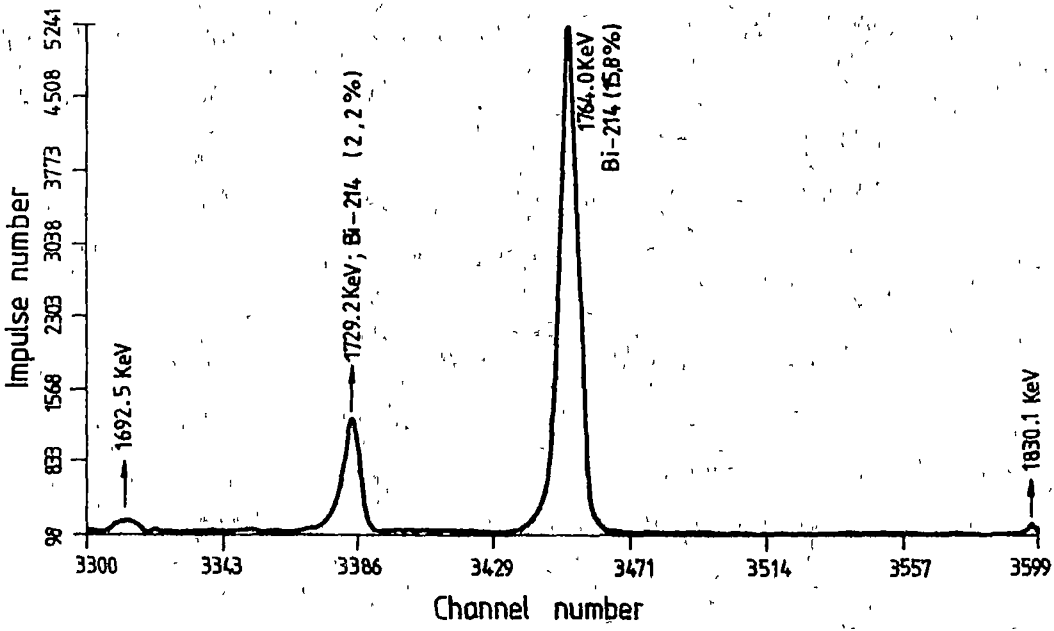

Fig.3

d. Radon group (^{222}Rn) includes isotopes from ^{222}Rn to ^{214}Po Equilibrium between ^{226}Ra and the head of this group ^{222}Rn is established in 38 days and between the members of the group in some hours. This group includes radioisotoprs: ^{222}Rn, ^{218}Po, ^{214}Pb, ^{214}Bi and ^{214}Po situated in the main sequence. Contribution to the gamma radioactivity of this group is given by ^{214}Pb (14%) and ^{214}Bi (83.6%). At the total radioactivity of uranium series this group contributes with 45% of alpha radioactivity, with 42% of betta radioactivity ant with 90-97% of gamma radioactivity. This group is the most important one from our point of view.

e. ^{210}Pb, the head of the fifth group, has a half-life period of 22.3 years, entering in equilibrum with the previous series after approximately 200 years and has ^{206}Pb as final product. The ^{210}Pb stays at the base of datind method of sediments of recent date.

The main equilibrium which may occur, in this series, is reffering to different geochemical migration of ^{238}U, ^{234}U, ^{226}Ra and ^{222}Rn [5,6].

Thorium family descendents have the half-life period relatively small and radioactive equilibrum in this series is practically permanent. From the point of view of gamma radiation energyes emited by the members of this series is remarked that of the ^{212}Pb, ^{212}Bi and ^{208}Tl radiosotopes.

In all quantitative measurements of U and Th must be had into consideration the question of radioactive equilibrum or nonnequilibrium in considered series. A special attention must be given, from this point of view, to radon and thoron [7, 8]. In the case, we are not sure on the equilibrum of ^{238}U - ^{226}Ra in the sample, it is possible to determine the ^{238}U content from the energy E = 1.015 MeV emited by ^{234}Th desintegration. This transition has a low probability (0.59%) and may be used in the case in which we have high resolution detectors, only. Method of trace detection [9, 10] is very indicated in radium determinations.

Because neither ^{238}U nor ^{232}Th do not emite gamma lines utile to active determination of these it is used the activity measurement of their desintegration products. When the equilibrium is brocken this matter is not possible. This situation appears when U and Th are exposed under chemical treatments conected to their purification. The equilibrium is established after six months in the ^{238}U - ^{234}Pa sequence and it takes more than 60 years in the ^{232}Th - ^{224}Ra sequence. Therefore, when are not considered the state of these equilibriums, the resulte of the measurements may be mistaken. In our case neither standarda nor sample were undertaken under chemical treatments and if someone may suppose that in then, there is a radioactive equilibrium. This fact is cheched by the results of our measurements. We must be sure in this case of the radon (^{222}Rn) and thoron (^{220}Rn) equilibrium.

Table 2 and 3 contain the experimental data quotationed from the computer memory for our UThS, in which from the total 45 peaks we retained 11 for uranium and 10 for thorium calculations.

The average of rations of R_U and R_{Th} were calculated with the formulae of weighted arithmetical average with the relative errors of individual ratio and the relative errors average with the formulae of armonical average. The relations of areas must be corrected for the different acquisition times and specifically R_U is multiplyed by 2.16 and R_{Th} is multiplyed by 2.00.

Table 2. Experimental data for the uranium determination.

Radio-isotope	E (keV)	A_s (imp)	ε_{st} (%)	A_{st} (imp)	ε_{st} (%)	$R_U(A_s/A_{st})$	Δ (%)
^{235}U	144	9.396	4	810	6	11.6	7.7
^{234}Pa	1.001	3.500	3.6	295	11	11.86	11.6
^{214}Pb	351.9	362.304	0.1	35.085	1.1	10.32	1.1
	242	94.030	0.4	9.105	3.5	10.32	3.52
^{214}Bi	609	243.600	0.2	23.056	1.3	10.56	1.31
	666	6.576	2.3	584	10	11.26	10.26
	767.7	19.470	1.0	1.942	7.4	9.96	7.46
	1.120	47.670	0.5	4.131	3.7	11.53	3.73
	1.237	17.037	1.0	1.388	8.5	12.28	8.55
	1.728	7.255	1.6	626	7.1	11.58	7.27
	1.764	36.210	0.6	3.098	3.7	11.68	3.74

$\overline{R}_U$ = 10.0126 $\overline{\Delta}$ = 3.17%

Table 3. Experimental data for thorium determination.

Radio-isotope	E (keV)	A_s (imp)	ε_{st} (%)	A_{st} (imp)	ε_{st} (%)	$R_{Th}(A_s/A_{st})$	Δ (%)
^{228}Ac	209.5	9.530	4.25	3.194	6.8	2.98	8.0
	269.8	15.120	2.03	3.927	7.0	3.85	7.3
	338.2	19.860	1.47	6.088	3.6	3.26	
	795.1	2.839	4.19	926	11	3.06	11.8
	911.1	18.185	1.08	5.475	2.6	3.32	2.8
^{212}Bi	238	100.260	0.48	33.267	1.1	3.01	1.2
	727.7	5.545	2.76	1.804	5.2	3.07	5.9
^{208}Tl	510.6	10.626	1.83	2.808	7.0	3.78	7.2
	583	27.815	0.87	8.479	2.6	3.28	2.74
	860	3.220	4.34	954	9.5	3.37	10.4

$\overline{R}_{Th}$ = 3.093 and $\overline{\Delta}$ = 3.89%

For the mass of U and Th from the UThS is obtained:

$M_U = R_U \cdot 2.16 M_{US} = (2.188 + 0.069)g$,

$M_{Th} = R_{Th} \cdot 2.00 M_{ThS} = (1.293 + 0.046)g$

and for the concentration the values:

$C_U = (M_U/M_S) \, . \, 100 = 1.271\%$,

$C_{Th} = (M_{Th}/M_s) \, . \, 100 = 0.70\%$,

where: $M_S = 171.67g$ is the UThS mass.

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BELTRAMI PARAMETRIZATION AND GAUGING OF VIRASORO AND W-INFINITY ALGEBRAS

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ABSTRACT. The gauging of Virasoro and w-infinity algebras are discussed from the point of view of BRST symmetry. Both algebras are realised as "Russian formulas" for the curvatures built from the generators of the Lie algebras and the corresponding gauge fields. The generalized curvatures are to determine the gauge invariant Lagrangians as well as the anomaly structures of the conformal two dimensional theory and the w-gravity.

1. Introduction. The two dimensional conformal field theory has the Virasoro as the underlying symmetry. The classical string action is a typical example of a theory invariant under the Virasoro algebra. Its invariance and its conformal properties are most clearly exhibited in terms of Beltrami differential /1-4/. In this parametrization the BRST agebra factorizes in two independent and separate structures, which implies that the ghost Lagrangian is a sum of a holomorphic and an antiholomorphic terms and the action for the string can be expressed ony in terms of Weyl invariant quantities.

However, any attempt to treat the spin two gauge field, i.e. the Beltrami differential, on the same footing as the higher spin fields, which occur in the w-gravity, does not have any future, since there are no higher-spin zweibein fields and any higher-spin Beltrami differential, with a similar geometric interpretation as the spin-2 zweibein field.

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On the other hand, in two dimension there is an alternative formulation /5, 6/ to describe the coupling of gravity to matter which includes the auxiliary fields J and $\bar{J}$. This alternative formulation has two advantages: on the one hand, it can be quite naturally connected with the gauging of the Virasoro algebra and, on the other hand, it does allow a natural extension for the higher spin gauge fileds. Which can be treated on the same footing as the spin 2 gauge field.

In this paper we shall adopt a very nice point of view, advocated in some recent papers by Baulieu, Bellon and Grimm /7-11/. We shall consider the Lie algebras as the starting point in our investigations, rather than considering them as special invariance properties of a given Lagrangian. For a given Lie algebra we associate a gauge field and a ghost to each generator of it and we build the corresponding BRST symmetry from a geometrical constrain on the curvature called the "Russian formula". This can be done very efficient if we use a Poisson bracket algebra realisation of the Lie algebra, which is possible not only for the Virasoro algebra but also for the w-infinity algebra. For using the Poisson bracket, in addition to the space dependence is convenient to introduce one (t) or two (t, u) additional variables. It seems that a modification of the Moyal bracket /12/ could be used instead of the Poisson bracket to obtain a realization of W-infinity algebra /13/.

The generalized one-form connection, constructed in the standard way /11/, will contain the Beltrami differential and the corresponding ghost for the Virasoro algebra and the high spin gauge fields and their ghosts for w-infinity algebra. This connection is fundamental object of our and it can be used to build up the gauge inveraint action, the possible anomalies and the Wess-Zumino action. For accomplishing these tasks it is necessary to introduce the matter fields. Furthermore, the gauging of left-moving and right-moving of w-infinity algebra, cannot be achieved by simply adding gauge field times current terms. The action in this case could be most conveniently written by introducing, once again, the auxiliary fields J and $\bar{J}$, which must be eliminated at the end of the calculation.

2. THE BELTRAMI DIFFERENTIAL AND THE VIRASORO ALGEBRA

2.1. The gauge fields. The Virasoro algebra, without the central charge, contains an infinite number of generators L_{-1}, L_0, L_1, ... which satisfy the following commutation relations:

$$[L_n, L_m] = (m - n)L_{m+n}; \ -1 \leq n,m < \infty \ . \qquad (1)$$

This Lie algebra can be realised very simple as a Poisson-bracket algebra of functions on a one-dimensional phase space, with the Poisson bracket defined as:

$$\{f,g\}_t = f\partial_t g - (\partial_t f)g, \qquad (2)$$

for two functions f(t) and g(t). Taking a basic set of functions

$$l_m = t^{m+1} \qquad (3)$$

we obtain the Virasoro agebra

$$\{l_n,l_m\}_t = (m - n)l_{m+n} \qquad (4)$$

The BRST symmetry is realised, in the ghost sector, by associating a ghost c_n, $n \geq -1$ to each generator L^n. In the general matrix representation (1) the ghost fields are gathered together in a Lie-valued ghost:

$$C = \sum_{n=-1}^{\infty} L^n C_n \tag{5}$$

which is not very convenient for the following since (5) contains the unknown generators L^n. However if use the basic (3) then the ghost c(t) has a simpler form:

$$C(t) = \sum_{n=-1}^{\infty} C_n t^{n+1} \ . \tag{6}$$

For a general Lie algebra, the BRST transformation of the ghosts c_a associated to it are given by:

$$sc^a = -\frac{1}{2} f^a_{bc} c^b c^c$$

where the coefficients f^c_{ab} are defined by

$$[T_a, T_b] = f^c_{ab} T_c$$

with T_a the generatoes of the Lie algebra. This BRST transformation can be rewritten in a simpler forms if one introduced the ghost $c = T_a c^a$

$$sc = -\frac{1}{2}[c, c] \ . \tag{7}$$

For the Virasoro algebra (4) the BRST symmetry takes the following compact form

$$sc + \frac{1}{2}\{c, c\}_t = 0 \ . \tag{8}$$

This BRST equation can be extended to include the gauge fields associated to generators L^n, for the Virasoro algebra we have found convenient to associate a one-form A^n. Furthermore, following Stora, we add the ghost number to the form degree and assume all commutators to be graded by this total degree. Therefore, we can combine the ordinary one-forms with ghost number zero and the zero-form with ghost number one i.e. $\tilde{A}^n = A^n + C^n$. For the Yang-Mills fields associated with a given algebra with the ghost satisfying Eq. (7) we can write "the Russian formula":

$$\tilde{F} = \tilde{\partial}\tilde{A} + \frac{1}{2}[\tilde{A},\tilde{A}] = F = dA + \frac{1}{2}[A,A]$$

where $\tilde{\partial} = d + s$ and $\tilde{A} = A + c$ with $A = A^a T_a$ is the Lie-values conection form. For the Virasoro algebra we clain that a similar formula takes place i.e.

$$\tilde{\partial}\tilde{A} + \frac{1}{2}\{\tilde{A},\tilde{A}\}_t = \tilde{\partial}\tilde{A} + \tilde{A}\partial_t\tilde{A} = o \qquad (9)$$

with

$$\tilde{A} = \sum_{n=-1}^{\infty} (A^n + C^n)\, t^{n+1} \qquad (10)$$

and $\tilde{\partial} = d + s$ with d the usual differentia.

Since the Virasoro algebra is deeply related to the two dimensional conformal symmetry, it is natural to try to connect the one-form A^n with the complex structure of a Riemanniann surface. Conformal classes of metrics on a Riemann surface can be parametrized by Beltrami coefficients $\mu(z,\bar{z})$ which are smooth complex valued function of the complex coordinates $(z,\bar{z})$ of the surface, with specific transformation properties. The complex coordinate $(Z,\bar{Z})$ corresponding to the complex structure parametrized by the Beltrami differential are given by the relations

$$dZ = \lambda[dz + \mu d\overline{z}] \text{ and } c.c. \tag{11}$$

Here λ and μ are smooth complex-values functions of $(z, \overline{z})$ which satisfy:

$$(\overline{\partial} - \mu\partial)\, z = 0 \quad \text{and } c.c. \tag{12}$$

$$(\overline{\partial} - \mu\partial)\,\lambda = (\partial\mu)\,\lambda \quad \text{and } c.c. \tag{13}$$

The infinitesimal diffeormorphism generated by the vector field $\xi\cdot\partial = \xi(z,\overline{z})\cdot\partial + \overline{\xi}(z,\overline{z})\overline{\partial}$ can be obtained with the Lie derivative $L_{\xi\partial} = i_{\xi\partial}d + di_{\xi\cdot\partial}$ acting on Z

$$\begin{aligned} \partial Z = L_{\xi\cdot\partial}Z = i_{\xi\partial}\cdot dZ = [\overline{\lambda}(dz + \mu d\overline{z})]\,(\xi\cdot\partial) = \\ = \lambda(\xi + \mu\overline{\xi}) = \lambda\cdot c\ , \end{aligned} \tag{14}$$

with $c = \xi + \mu\overline{\xi}$. By evaluation the variation of dZ in two ways δ(d Z) = d(δ Z) we can get the induced variation of μ:

$$\delta\mu = [\overline{\partial} - \mu\partial + (\partial\mu)]\, c\ . \tag{15}$$

If we identify c in (14) with the ghost vector field of two dimensional diffeomorphism, we can identify Eqs. (14) and (15) with the definition of the BRST differential s

$$sZ = \lambda c; \quad s\mu = [\overline{\partial} - \mu\partial + (\partial\mu)]\, c\ . \tag{16}$$

The nilpotency of s requires

$$sc = c\partial c \tag{17}$$

Now the equation (9) for ghost number zero and one and for t = 0 gives:

$$\begin{gathered} dA^{-1} + A^{-1}A^{0} = 0 \\ sA^{-1} + dc^{-1} + A^{-1}c^{0} + c^{-1}A^{0}. \end{gathered} \tag{18}$$

Comparing Eqs. (18) and (17) we can easily see that a possible solutions of these equations:

$$A^{-1} = dz + \mu d\overline{z}; \quad c^{-1} = c;$$

$$A^0 = (\partial\mu)\,d\bar{z}; \quad c^0 = \partial c \, . \tag{19}$$

The rest of the one-forms A^n and the ghosts c^n can be found out by imposing the validity of Eq.(9) for all values of t /11/. On the other hand, we can sove Eq. (9) by making a gauge choice

$$\tilde{A} = dz + d\bar{z}\tilde{A}_{\bar{z}}\;(z,\bar{z},t) + \tilde{c}(z;\bar{z},t)\;\; . \tag{20}$$

With this choice Eq. (9) yields

$$\frac{\partial}{\partial z}\tilde{A}_{\bar{z}} = \frac{\partial}{\partial t}\tilde{A}_{\bar{z}}\;;\;\; \frac{\partial}{\partial z}\tilde{c} = \frac{\partial}{\partial t}\tilde{c}.$$

equations which have the obvious solution

$$\begin{aligned}\tilde{A} &= dz + d\bar{z}A_{\bar{z}}\,(z+t,\,\bar{z}) + c(z+t,\bar{z}) = \\ &= e^{t\,\partial_z}[dz + d\bar{z}\mu + c]\;.\end{aligned} \tag{21}$$

2.2. Virasoro Invariant Lagrangian. From the field $\tilde{A}$ one could construct an invariant if one looks for a two-form $\mathfrak{L}$, which is $\tilde{d}$-closed and it is defined up to $\tilde{d}$-exact terms. The ghost zero part of $\mathfrak{L}$ is a possible BRST-invariant Lagrangian. The only possible candidate built only from A is $\tilde{A}\tilde{\bar{A}}$, which nevertheless is not $\tilde{d}$-closed since $\tilde{A}$ satisfies Eq. (9). Here $\tilde{\bar{A}}$ is the complex conjugate of $\tilde{A}$. Therefore, in order to build up an invariant Lagrangian we must couple $\tilde{A}$ to a new field, the matter filds.

The matter fields are zero-forms, which cannot contain ghosts. For our purpose the starting point is the equation (11). In two-dimension, there is a possibility to describe the coupling of gravity to matter fielld, which includes two auxiliary fields

J and $\bar{J}$ /5/. The matter field in this aproach is described by a scalar field, which we will take to be a scalar field, which we will take to be a single real scalar φ.

We will suppose that the real field φ and $(J, \bar{J})$ are conected by the equation

$$d\varphi = JA^{-1} + \bar{J}\bar{A}^{-1} \tag{22}$$

i.e. the field φ, J and μ are related by:

$$\begin{aligned} J &= \partial\varphi - \bar{\mu}\bar{J} \\ \bar{J} &= \bar{\partial}\varphi - \mu J. \end{aligned} \tag{22'}$$

The auxiliary field J could be considered as the first term in a set of zero forms $J^{(n)}$ with $n \geq -1$, which we assemble into:

$$\tilde{J} = \sum_{n=-1}^{\infty} t^{n+1} \cdot J^{(n)} \tag{23}$$

and the equation (22) can be extended for the tilde fields as:

$$\tilde{d}\tilde{\varphi} = \tilde{J}\tilde{A} + \tilde{\bar{J}}\tilde{\bar{A}} \ . \tag{24}$$

Applying $\tilde{d}$ to this equation and using $\tilde{d}^2 = 0$ we get

$$(\tilde{d}\tilde{J})\tilde{A} + \tilde{J}(\tilde{d}\tilde{A}) + c.c. = 0. \tag{25}$$

The action of the BRST symmetry on $\tilde{\varphi}$ and $\tilde{J}$ can be read off from Eqs. (24) and (25). The equation (24) can be fulfilled whether one imposes the condition for vanishing of the curvature of $\tilde{J}$:

$$\tilde{d}\tilde{J} + \{\tilde{A}, \tilde{J}\}_t = 0. \tag{26}$$

With the gauge choice (21) eq. (26) yields

$$\tilde{J} = J(z + t, \bar{z}) \tag{27a}$$

and

$$\left(\frac{\partial}{\partial \bar{z}} - A_{\bar{z}} \frac{\partial}{\partial t}\right) \tilde{J} = \tilde{J} \cdot (\partial_z A_{\bar{z}}) \ . \tag{27b}$$

For t = 0 eq. (27b) coincides with eq. (13) i.e. we can identify J with λ and φ with $Z+\bar{Z}$.

With $\tilde{\mathcal{J}}$ and $\tilde{A}$, it is quite easy to construct a BRST invariant action as the real two-form

$$\mathfrak{L} = (\mathcal{J}\tilde{A})(\bar{\tilde{\mathcal{J}}}\bar{\tilde{A}}) \quad . \tag{28}$$

One can indeed verify that

$$\partial\mathfrak{L} = 0,$$

which proves that the ghost zero part of $\mathfrak{L}$ is a BRST-invariant two-form. Now whether we take into consideration eq. (22) the classical Lagrangian, obtained from (28) for t = 0 has the usual form:

$$\mathscr{L}_{ce} = \frac{1}{2}\,\frac{1}{1-\mu\cdot\bar{\mu}}\,(\partial\varphi - \bar{\mu}\bar{\partial}\varphi)\,(\bar{\partial}\varphi - \mu\partial\varphi) \tag{29}$$

In fact, in the gauge we have considered, t occurs only through z + t and after integration, the action does not depend on it. Therefore, the Virasoro gauge theory reduces, rather naturally, to the two dimensional conformal field theory.

2.3. Virasoro covariant anomalies. The Wess-Zumino action. In this formulation of the Virasoro gauge field theory the general forms of the consistent and covariant anomalies can be determined rather straightforwardly. Besides, the Wess-Zumino action has a simple form and is calculated very easily. As it is well known, in the BRST formalism, an anomaly for the Virasoro algebra is a two form with ghost number one. A convariant anomaly is an anomaly which has a covariant form and therefore it is well defined on the whole Riemann surface.

Thus, in order to find an anomaly, one must look for a general (i.e. including the ghosts) three form $\tilde{\Delta}_3$ satisfying $\tilde{\partial}\tilde{\Delta}_3 = 0$. A solution of this equation was proposed by Baulieu, Bellon and Grimm /11/ and it has the form

$$\tilde{\Delta}_3 = \tilde{A}\ \dot{\tilde{A}}\ \ddot{\tilde{A}}, \tag{30}$$

where a dot means the derivative with respect to t. In the gauge (21) $\tilde{\Delta}_3$ has its ghost one part given by

$$A(c,\mu) = -\partial c\, \partial^2 \mu\, dz \wedge \partial \bar{z} \tag{31}$$

for t = 0, which is the diffeomorphism anomaly obtained in a factorized form /2,3/.

The form of A is not well defined on the whole Riemann surface since it does not have an covariant form under a conformal charge of coordinate z → z'(z).

To obtain the covariant form of the anomaly, we might follow the algebraic approach proposed by Abud, Gieres and Noirot /14,15/. However, we have found rather difficult the implementation of these ideas for the Virasoro algebra. So, at this point we will just follow the general prescription for the covariantisation on a generic Riemann surface. In fact, the anomaly (31) is equivalent to

$$A = c\partial^3 \mu\, dz \wedge \partial z \tag{31'}$$

and it involves the third order differential operator ∂^3. This expression is not well defined on a generic Riemann surface since the integrand does not transform with the Jacobian upon passage from one coordinate chart to another. In fact the modified expression

$$\tilde{A} = c[\partial^3 + (R\partial + \partial R)]\mu \tag{32}$$

with R, a projective connection, given by

$$R = \partial^2 \ln\lambda - \frac{1}{2}(\partial \ln\lambda)^2, \tag{33}$$

transforms with the Jacobian and represents the covariant anomaly. We believe that this form of the anomaly can be obtained by using the general algebraic methods for the covariant anomaly.

Since the Virasoro algebra is closed connected to the general coordinate transformations, which define a non-comutative group, the construction of the associated Wass-Zumino action represents a serious problem. However, for the factorized anomaly, the problem is simpler. This factorized anomaly could be obtained from $\tilde{\Delta}_3$ by using the standard procedure /17/. In fact we have to "kill" the anomaly A by enlarging the space of fields. We shall lift the whole construction from the Rieman surface M to Mx[0,1] by considering a family of Beltrami differentials μ_u such that $\mu_0 = 0$ and $\mu_1 = \mu$ and a family of the "Goldstone field" which taked its values in the group of diffeomorphisms and $\varphi_0 =$ identity and $\varphi_1 = \varphi$. The field $\tilde{A}$ and the differential are replaced in this case by

$$\check{A} = \tilde{A} + a du; \; d_{tot} = \tilde{\partial} + du.$$

The function a is determined form Eq. (9) written in terms of the new fields and differentials. The Wess-Zumino action for the Virasoro algebra (30) is the ghost zero part of the three-form $\check{\Delta}_3(\check{A}^{\varphi})$ with $\check{A}^{\varphi}$ the field obtained from $\check{A}$ by the action of the diffeomorphism φ. If we integrate out the auxiliary variable u, one finds the following form of the Wess-Zumino action:

$$\mathcal{L} = \frac{1}{2}\, dz \wedge d\bar{z}\, (\mu^{\varphi} \partial^2 \ln \lambda^{\varphi} - \mu \partial^2 \ln \lambda)$$

which takes the form given by Polyakov /18/

$$\mathcal{L} = -\frac{1}{2}\, dz \wedge d\bar{z}\, \mu \partial^2 \ln \lambda \tag{34}$$

if φ is restricted by the condition $\mu^{\varphi} = 0$.

It is worth pointing out that the form (34) of the WZ can be written with the one-form $\tilde{A}$ and co called "half Liouville filed" L /13/. The field L is a matter field, which has the first term in the t expansion just ln λ, with λ define in (13) and which fulfils the equation

$$dL + A\, \partial_t L - \partial_t A = 0 .$$

With this definition we can find out, by a simple inspection, that the two-form

$$\mathcal{L} = -L \tilde{A} \ddot{A} \tag{35}$$

satisfies the equation $\partial \mathcal{L} = \Delta_3$ i.e. its zero ghost part is the WZ action for the Virasoro algebra. In fact, it is easy to see that the ghost number zero of $\mathcal{L}$ coincides with (34).

3. W-INFINITY ALGEBRA

3.1. The fields. The $W_{1+\infty}$ algebra is an extension of the Virasoro algebra on the one hand, and a limiting case of the W-infinity algebra, on the other hand /18/. It can be written in the following simple form:

$$\left[L_n^i, L_m^j\right] = [(i+1)m - (j+1)n]\, L_{m+n}^{i+j} \tag{36}$$

This algebra admits an algebraic interpretation, as the algebra of smooth symplectic, area-preserving, diffeomorphisms of a cylinder. This can be easily seen considering a set functions /19/:

$$U_m^l = + i\, e^{mx} y^{l+1}$$

on a cylinder $S^1 \times \mathbf{R}$, with $0 \le x \le 2\pi$, $-\infty < y < +\infty$. These functions form a complete set if $-\infty < m < +\infty$ and $l \ge -1$. The symplectic structure is generated by the Poisson bracket

$$\{f,g\}_{x,y} = \frac{\partial f}{\partial n}.\frac{\partial g}{\partial y} - \frac{\partial f}{\partial y}.\frac{\partial g}{\partial x}. \tag{37}$$

and the area preserving transformation are generated by $\delta x^{\mu} = \{\Lambda, x^{\mu}\}$ ($\mu = 1, 2$) where Λ is an arbitrary function. One can see that the basis $\{u_m^l\}$ satisfies the $w_{1+\infty}$ algebra:

$$\{u_m^i, u_n^j\} = [(i+1)m - (j+1)n]\, u_{m+n}^{i+j}. \tag{38}$$

The ghost sector of the BRST symmetry for this algebra can be constructed in a similar manner with the Virasoro case. Here we shall use the basis

$$l_n^i = t^{n+1} u^{i+1}$$

instead of u_n^i and we define the ghost

$$C = \sum_{n,i=-1}^{\infty} t^{n+1} u^{i+1} c_i^{n-i}$$

with c_n^i the ghost associated to the generater L_n^i.

The Virasoro case (8) can be extended for the w-infinity algebra in a straightforward way. The BRST symmetry of the ghosts has now the form

$$sc + \frac{1}{2}\{c,c\}_{t,u} = 0. \tag{39}$$

This equation can be extended to include the gauge fields associated to the generators L_n^i. We can assemble all these fields into a power series

$$\tilde{A}_0 = \sum_{u,l=-1}^{\infty} T^{n+1} u^{l+1} A_l^{u-l}$$

where A_n^i is a one form attached to the generator L_n^i which contains the gauge fields. Moreover, for the complete one-form

$$\tilde{A} = \tilde{A}_0 + C$$

it has been proposed /11/ the equation

$$\tilde{\partial}\tilde{A} + \frac{1}{2}\{\tilde{A},\tilde{A}\}_{t,u} = 0. \qquad (40)$$

where $\tilde{\partial} = d + s$. This equation contains eq. (39) for the ghost number two.

As in the Virasoro case, we can chose a special gauge and identify the physical gauge fields. If one identifies A_0^{-1} as the Beltrami differential, then the equation (40), which is equivalent to the BRST symmetry for w-infinity algebra, has the solution /11/:

$$\tilde{A} = u dz + \sum_{l=-1}^{\infty} u^{l+1}(A_l(z+t)\,d\bar{z} + c_l(z+t)) \qquad (41)$$

where A_l is the complex gauge field, coupled to the spin-(l+2) conserved current in the w-gravity, and c is the corresponding ghost. The BRST transformations for these fields can be obtained from eq. (40) and are given by

$$sA_l = \sum_{j=0}^{l=1} [(j+1)A_j\partial c_{l-j} - (l-j+1)C_{l-j}\partial A_j]$$
$$sc_l = \sum_{j=0} (j+1)\, c_j \partial c_{l-j}.$$

3.2. Action for W-gravity. There are a relative small number of realisations for w-infinity algebra by gauging it, in comparison to the more known classes realisations of Virasoro algebra, despite the kindship between the two. Gauging this algebra we obtain W-gravity. As in the Virasoro case, a BRST - invariant action cannot be constructed only with the field $\tilde{A}$. However, the auxiliary fields $\bar{J}$ and J and the scalar field φ are introduced here in a different manner. For w-gravity, we replace eq. (22) by

$$\partial\varphi = \tilde{A}(J) + \tilde{\bar{A}}(\bar{J}) \tag{43}$$

where

$$\tilde{A}(J) = \tilde{A}(u-j, t, z, \bar{z}) = J dz + \sum_{l=-1}^{\infty} (d\bar{z} A_l + C_l) J^{l+1}.$$

From this equation we can obtain the BRST transformations of φ and J and $\bar{J}$, the relations between these fields since this equation is equivalent to the following ones:

$$s\varphi = \sum_{l=-1}^{\infty} (J^{l+1} C_l + \bar{J}^{(l+1)} \bar{C}_l) \tag{44}$$

$$J = \partial\varphi - \sum_{L=-1}^{\infty} \bar{A}_1 \bar{J}^{l+1}$$

$$\bar{J} = \bar{\partial}\varphi - \sum_{l=-1}^{\infty} A_1 J^{l+1} \tag{45}$$

The BRST transformations of the auxiliary fields J and $\bar{J}$ and the compatibility of eqs.(45) can be obtained from eq. (43) by using the nilpotence of ∂ i.e. $\partial^2 = 0$. In this way we obtain

$$\partial J = \partial\tilde{A}(J) \text{ and } c.c.$$

i.e.

$$sJ = \sum_{l=-1}^{\infty} \partial (C_l J^{l+1})$$

and

$$\bar{\partial} J = \sum_{l=-1}^{\infty} [(l+1) A_l J^l + (\bar{\partial} A_l) J^{l+1}] .$$

It is worth while to point out that eqs. (45) could be considered the equation of motion for the auxiliary fields J and $\bar{J}$, given by the action

$$\mathcal{L} = -\frac{1}{2}(\partial\varphi)(\bar{\partial}\varphi) - J\cdot\bar{J} + (\bar{\partial}\varphi) J + (\partial\varphi)\bar{J} - \\ - \sum_{l=1}^{\infty} \frac{1}{l+2}(A_l J^{l+2} + \bar{A}_l \bar{J}^{l+2}) \qquad (46)$$

which describes the coupling of the gauge fields A_l to the spin-(l+2) conserved current $(\partial\varphi)^{l+2}$.

The Lagrangian (46) can be extended to describe W_N gravity /22/. If one replaces in $\mathcal{L}$ the scalar field φ and the auxiliary fields J and $\bar{J}$ with a set of scalar fields that take their values in the Lie algebra of SU(N), then, although the entire w-algebra is realised as a symmetry, it is really only the gauge fields A_l, $l \leq N-1$ that play an essential role. The rest of the gauge fields can be set to zero by means of additional symmetries of the Lagrangian, that are of the Stueckelberg type. Therefore, in this case the remaining fields give rise to a non-trivial gauging of the W_N algebra.

The BRST invariance of $\mathcal{L}$ given by (46) can be checked by using the BRST transformations of the fields A_l, φ and J. Nevertheless, it is desirable to obtain an action which is d-closed and with the ghost zero part just $\mathcal{L}$. For this we will introduce a new one-form.

$$\tilde{B}(J) = \frac{1}{2}\partial dz + \sum_{l=-1}^{\infty} (A_l d\bar{z} + C_l)\frac{1}{l+2} J^{l+1} \tag{47}$$

which seems to be the "integral" of $\tilde{A}(J)$. The action which is d-closed and has the ghost zero part just L has the form

$$\mathfrak{L} = \frac{1}{2}\tilde{A}(J)\bar{\tilde{A}}(J) - [\tilde{A}(J)\tilde{B}(J) + \bar{\tilde{A}}(J)\bar{\tilde{B}}(J)] \tag{48}$$

Indeed, on the one hand, the ghost zero part of $\mathfrak{L}$ is

$$\mathfrak{L} = \frac{1}{2}\left[J\bar{J}\left(1 - \left|\sum_{l=1}^{\infty} A_l J^{l+1}\right|^2\right) + \sum_{l=-1}^{\infty}\frac{1}{l+2}(A_l J^{l+2} + \bar{A}_l \bar{J}^{l+2})\right].$$

If we take into account the relations (45), this Lagrangian boils down to (46). On the other hand L is d-closed, fact which can be verified by a direct computation and the use of the form of dJ.

3.3. W-anomaly. As for the Virasoro algebra, we shall find, by inspection, a $\tilde{\partial}$-closed form, which depends on A_l and c_l. It is easy to verify, that the looking for three-form can be chosen in this case as /11/:

$$\tilde{\Delta}_3 = \tilde{A}\partial\tilde{A} \tag{49}$$

The closeness $\tilde{\Delta}_3$ can be verified by using eq. (40). In the gauge (41) the ghost part of $\tilde{\Delta}_3$ for t = u = 0 takes the simple form

$$\Delta_2^1 = (A_{-1}\partial C_{-1} - C_{-1}\partial A_{-1})\, dz \wedge d\bar{z}, \tag{50}$$

which is invariant under holomorphic coordinate transformations. However this part of the anomaly is just the first term in a much more complicated expression obtained by Hull /20/ and K. Li and Pope /21/.

A possible solution of this problem seems to be connected to the definition of trace for the auxiliary variables t and u. In order to get rid of these variables we must add a "trace" in front of the anomaly, which means either putting t = u = 0 after doing all differentiations with respect to them, or integration in a special way over t and u. If one wants to follow, as close as possible, the Yang-Mills case, we shall try to write the anomaly in a w-infinity basis. Since in the YM case anomaly $\Delta(c,A)$ is written as:

$$\Delta(c,A) = Tr(c\,G(A)) = C_a G_b\, Tr\,(T^a T^b)$$

it seems natural to try to write our anomaly in the same form. With a suitable definition of the trace, we can suppose that

$$Tr(u_m^i\ u_n^j) \pm \delta^{ij}\delta_{mn} \tag{51}$$

Therefore the anomaly Δ_2^1 takes the form

$$\Delta_2^1 = \sum_{l=-1}^{\infty} a_l (A_l \partial^{2l+1} c_l - c_l \partial^{2l+1} A_l)\, dz \wedge d\bar{z}$$

with a_l certain coefficients. This form of the anomaly has the same form as the one given by C. Hull /20/. However the form and the interpretation of these anomaly structures deserve further study.

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MAGIC ANGLE SPINNING AND POLARIZATION TRANSFER IN SYSTEMS WITH RESOLVED HETERONUCLEAR INTERACTIONS

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ABSTRACT. - Thermodynamic aspects under fast magic angle sample spinning for ferocene are studied. An extension of the static cross-polarization model is presented which applies to the "sidebands" of the Hartmann-Hahn condition. The S-spin magnetization in a CP experiment as function of the S-spin irradiation ω_{1s} is calculated (CP-MAS spectrum).

1. Introduction. High-speed spinning at the magic angle can significantly modify the rate of polarization transfer from abundant to rare spins in an cross-polarization NMR experiment on solid, if the spinning speed is greater than or comparable to the static dipole-dipole interaction among abundant spins in the rotating frame in a spin-lock(SL) experiment [1]. We consider in the following the "fast spinning" limit where the MAS (magic-angle spinning) frequency $\omega_r/2\pi$ exceeds the proton-proton interaction ($\omega_r >> b_{kj}$). The basic phenomena were demonstrated by Waugh et al. [1], the Hartmann-Hahn condition [2] is split into sidebands appearing at the Hartmann-Hahn match plus or minus integer multiples of the MAS frequency $\omega_{Ir} = \omega_{1s} \pm n\omega_r$ [3] with $\omega_{1I} = -\gamma_I B_{1I}$ and $\omega_{1s} = -\gamma_s B_{1s}$. For sufficiently fast spinning the sidebands for n = ±1 and ±2 dominate the spectrum. At the sideband position, the secular dipolar terms exist in the interaction Hamiltonian causing polarization transfer.

In the following we refer to the observed S-spin magnetization in a CP-experiment as function of strength of the

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S-spin irradiation ω_{1S} as the "CP spectrum". We consider an organic solid by ferocene $[(C_5H_5)_2Fe]$ single crystal with short covalent bonds between ^{13}C and ^{1}H nuclei.

In the case of an S spin with a strong coupling to a spin I_1 both spins being coupled more modestly to the remaining spins I_k $(k > 1)$, the system is treated satisfactorily [4] as the tightly coupled spin pair immersed in a bath consisting by the remaining protons. We describe the dynamics of CP-MAS process in two stages. First we treat the spin pair alone, then we allow the spin pair to come into thermodynamic contact with remaining spins and discuss the quasi-equilibrium which is reached.

2. The isolated spin pair Hamiltonian. The Hamiltonian of the spin pair I_1-S in the usual doubly rotating tilted frame, for strong resonant rf field applied along the X axis of the rotating frame, is given by [4]:

$$H_{pair} = \omega_{1I} I_{1z} + \omega_{1S} S_z + b_1(t)\, 2 I_{1y} S_y \tag{1}$$

where $b_1(t)$ is dipolar coupling constant and its time dependence is caused by the sample rotation.

For a static sample it is time independent and given by

$$b_1 = \frac{1}{4}\delta_1 (3\cos^2\theta_1 - 1)$$

with the anisotropy of the dipolar coupling

$$\delta_1 = -2\,\frac{\mu_0 \gamma_I \gamma_S}{4\pi r_1^3}$$

Here r_1 is the I_1-S internuclear distance and θ_1 the angle between the internuclear vector and the static magnetic field B_0.

Magic angle spinning leaves invariant the spin part of the

Hamiltonian but renders the dipolar coupling constants time dependent. If θ^r and φ^r denote the polar angles that relate the internuclear vector to the MAS rotation axis and $\omega_r/2\pi$ to the MAS frequency, the dipolar coupling constant is given by:

$$b_1(t) = \frac{1}{2}\delta_1[(1/\sqrt{3})\exp(i\omega_r t)\,C_{21}(\theta^r,\varphi^r) - (1/\sqrt{3})\exp(-i\omega_r t)\,C_{2-1}(\theta^r,\varphi^r)$$
$$+ (1/\sqrt{6})\exp(2i\omega_r t)\,C_{22}(\theta^r,\varphi^r) + (1/\sqrt{3})\exp(-2i\omega_r t)\,C_{2-2}(\theta^r,\varphi^r)]$$

where C_{kg} are the modified spherical harmonics

$$C_{kg}(\theta^r,\varphi^r) = \sqrt{4\pi/(2k+1)}\,Y_{kq}(\theta^r,\varphi^r)\ ,\ k,g=1,2$$

To be able to apply thermodynamics properly to the MAS case, we have to approximate the time - dependent Hamiltonian of Eq. (1) by a time independent Hamiltonian H^o because the rules of thermodynamics apply only to conservative systems. One way to achieve this is to calculate the average Hamiltonian in an appropriate interaction frame and to neglect the nonsecular or time dependent parts of the interaction Hamiltonian [3]. If we describe the CP-MAS experiment in the doubly tilted rotating frame, the reservoir terms remain time independent under MAS but the perturbation V, containing the heteronuclear dipole coupling, become time dependent. The perturbation Hamiltonian V(t) has frequency components at ω_r and $2\omega_r$. For n = -2, -1, 1, 2 (the sidebands of the CP spectrum) the transition frequencies of a heteronuclear process is matched by a frequency component of V(t). We transform therefore to a rotating coordinate system where the resonant part of V(t) becomes time independent. A such transformation can be made using a transformation operator

$$U = \exp(in\,\omega_r t S_z) \qquad (2)$$

After a such transformation the perturbation can be decomposed into a time dependent and a time independent contribution V(t) = V_0 + $V_1(t)$. The time dependent part of the perturbation contains frequencies at integer of the new reservoir Hamiltonian. The full Hamiltonian can be written as:

$$H^T_{pair} = \omega_{1I}I_z + (\omega_{1s} - n\omega_r)S_z + \frac{\delta_1}{2\sqrt{2}}\sin 2\theta^r\Big[\frac{1}{4}\exp(i\varphi^r)(S^+I_1^- - S^+I_1^+) + \frac{1}{4}\exp(-i\varphi^r)(S^-I_1^+ - S^-I_1^-)\Big] \tag{3a}$$

for n = ±1 and

$$H^T_{pair} = \omega_{1I}I_z + (\omega_{1s} - n\omega_r)S_z + \frac{\delta_1}{2\sqrt{2}}\sin^2\theta^r\Big[\frac{1}{4}\exp(2_i\varphi^r)(S^+I_1^- - S^+I_1^+) + \frac{1}{4}\exp(-2i\varphi^r)(S^-I_1^-)\Big] \tag{3b}$$

for n = ±2 case. In the following we can take for φ^r a particular value $\varphi^r = 0$ and will be obtained for full Hamiltonian

$$H^T_{pair} = \omega_{1I}I_z + (\omega_{1s} - n\omega_r)S_z + \frac{\delta_1}{4\sqrt{2}}\sin 2\theta^r(2I_{1y}S_y) \tag{4a}$$

for n = ±1 case, and

$$H^T_{pair} = \omega_{1I}I_z + (\omega_{1s} - n\omega_r)S_z + \frac{\delta_1}{4\sqrt{2}}\sin^2\theta^r(2I_{1y}S_y) \tag{4b}$$

for n = ±2 case. It may be separated in two commuting parts [4]

$$H^T_{pair} = H^T_\Sigma + D^T_\Delta \tag{5}$$

with

$$H^T_\Sigma = \omega^\Sigma_e I^\Sigma_e, \quad H^T_\Delta = \omega^\Delta_e I^\Delta_e,$$

$$\omega^\Sigma_e = \left[(\tilde{\omega}_{1s} + \omega_{1I})^2 + (a_1)^2\right]^{1/2}, \quad \omega^\Delta_e = \left[(\tilde{\omega}_{1s} - \omega_{1I})^2 + (a_1)^2\right]^{1/2}$$

$$I^\Sigma_e = I^\Sigma_z\cos\theta^\Sigma + I^\Sigma_x\sin\theta^\Sigma,$$

$$I^\Delta_e = I^\Delta_z\cos\theta^\Delta + I^\Delta_x\sin\theta^\Delta,$$

$$I^\Sigma_z = \frac{1}{2}(I_{1z} + S_z), \quad I^\Delta_z = \frac{1}{2}(I_{1z} - S_z),$$

$$I^\Sigma_x = \frac{1}{2}(I_1^+S^+ + I_1^-S^-), \quad I^\Delta_x = \frac{1}{2}(I_1^+S^- + I_1^-S^+),$$

$$\tilde{\omega}_{1s} = \omega_{1s} - n\omega_r,$$

where

$$a_1 = \frac{\delta_1}{4\sqrt{2}} \sin^2\theta^r \,, \quad n = \pm 1$$

$$a_1 = \frac{\delta_1}{4\sqrt{2}} \sin^2\theta^r \,, \quad n = \pm 2$$

and

$$\mathrm{tg}\,\theta^\Sigma = a_1 / (\omega_{1I} + \tilde{\omega}_{1S})$$

$$\mathrm{tg}\,\theta^\Delta = a_1 / (\omega_{1I} - \tilde{\omega}_{1S}) = -b_1 / \Delta\omega$$

The eigenvalues of H^T_{pair} are $\pm\frac{1}{2}\omega_e^\Sigma$ and $\pm 1/2\,\omega_e^\Delta$ and the spin pairs may be treated as two independent two-level systems involving the inner and outer pair of energy levels and representing the zero and double quantum frame, respectively.

3. Modified thermodynamic theory for resolved heteronuclear coupling. We assume in the following that the initial spin density operator $\sigma(o)$ is prepared as

$$\sigma(o) = \left(1 - \frac{t_1\omega_{0I}}{kT_1} \sum_{k=1}^{NM} I_{kx}\right) / T_r\{1\} \tag{6}$$

by a initial $(\pi/2)_y$ pulse on the I spin applied to a system in thermal equilibrium at the high lattice temperature T_L, in the static field B_0. Defining

$$\alpha_{0I} = -\frac{t_1\omega_{0I}}{kT_L T_r\{1\}}$$

the initial density operator in the tilted rotating frame is

$$\sigma^T(o) = \alpha_{0I} \sum_{k=1}^{N+1} I_{kz} \tag{7}$$

Because the spin pair treated in the last section interact with the surrounding protons and will tend to reach thermal equilibrium through spin diffusion, the quasi-equilibrium density operator $\sigma^T(\tau_{ge})$ can be represented [4] as the projection of the operator $\sigma^T(o)$ to a three-dimensional space defined by three orthogonal quasi-invariants $\{ Q_1, Q_2, Q_3 \}$:

$$\sigma^T(\tau_{ge}) = \alpha_{0I} \sum_{i=1}^{3} a_i Q_i \tag{8}$$

We suppose that the set of operators Q_{ii} may be chose such that Q_i are orthogonal

$$< Q_i | Q_j > = 0, \quad i \neq j$$

where $< A|B > = Tr\{A^+ B\}$. they are

$$Q_1 = \frac{1}{N+2} (\omega_e^\Sigma + N\omega_{1I}) \, (2 I_e^\Sigma + \sum_{k=2}^{N+1} I_{kz}) , \tag{9}$$

$$Q_2 = \frac{1}{N+2} (\omega_e^\Sigma - 2\,\omega_{1I}) \left(N I_e^\Sigma - \sum_{k=2}^{N+1} I_{kz} \right) , \tag{10}$$

$$Q_3 = -\omega_e^\Delta I_e^\Delta , \tag{11}$$

because the homonuclear I-I spin dipolar interactions are neglected as following by magic angle sample spinning.

Assuming now a strong rf field $|\omega_{1s} + \omega_{1I}| >> |a_1|$ and making the approximation $\omega_e^\Sigma \approx \tilde{\omega}_{1S} + \omega_{1I}$ the coefficients a_i are evaluated from the condition

$$\alpha_{0I} a_i = \frac{< \sigma^T(0) \, | \, Q_i >}{< Q_i \, | \, Q_i >} \tag{12}$$

as

$$a_1 = \frac{N+1}{\tilde{\omega}_{1S} + (N+1)\, \omega_{1I}}$$

$$a_2 = -\frac{1}{\Delta\omega}$$

$$a_3 = -\frac{1}{\omega_e^\Delta} \cos\theta^\Delta .$$

The quasi-equilibrium density operator become

$$\sigma^{T}(\tau_{ge}) = \alpha_{oI}\left\{I_{e}^{\Sigma} + \sum_{k=2}^{N+1} I_{kz} + I_{e}^{\Delta}\cos\theta^{\Delta}\right\} \tag{13}$$

From this expression the quasi-equilibrium value of $<S_x>$ is

$$\langle S_x\rangle = \langle S_z\rangle^{T} = \frac{t_1\omega_{0I}}{8KT_L}\cdot\frac{a_1^2}{(\omega_{1s}-n\omega_r-\omega_{1I})^2}+a_1^2 \tag{14}$$

and we observe that the Hartmann-Hahn condition for a static sample, $\omega_{1s} = \omega_{1I}$ splits for MAS into a series of new matching conditions $\omega_{1s} + n\omega_r = \omega_{1I}$ where $n = \pm 1, \pm 2$.

4. Conclusions. Intensity of the carbon signal in an organic solid by ferocene after a CP magic angle sample spinning experiment has been calculated by a modified CP model. The maximum of cross-polarization will be obtain for a modified Hartmann-Hahn condition $\tilde{\omega}_{1s} = \omega_{1I}$, obtaining a split of CP-spectrum. The "sidebands" are located at the Hartmann-Hahn condition plus or minus multiples of the MAS frequency.

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THE THERMAL INSTABILITY OF A MAGNETOFLUID IN A VERTICAL CHANNEL IN THE PRESENCE OF A RADIATION EFFECT

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ABSTRACT. - This paper studies the effect of radiation on the free convection flow of an electrical conducting viscous fluid througnh an open-ended vertical channel and permeated by a constant magnetic field in transverse direction. The temperature of walls has supposed to vary linearly with the distance. In the first paper we obtains the expression of amplitude disturbance of velocity.

Introduction. The problem of heat transfer in electrically fluids permeated by electromagnetic fields have been studied by many authors [1], [2], [3]. Such studies are of a great importance in the design of magnetohydrodynamic generators, shoks tubes, pumps, etc. The comprerhensive review of which has been given by Romig [4].

The purpose of this paper is to studies the instabilities of an electrically fluid confined in an open-ended vertical channel in the presence of an magnetic field perpendicular to the direction of flow, taking in account the radiaton effect.

Basic equations and the problem. We consider a layer of an electrically viscous fluid within a vertical open-ended channel is heated from below and in the presence of a radiation effect. An horizontal uniform magnetic field $\vec{B}_0$ is applied normally to one side of channel walls. In this model we are not concerned

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with the forced convection [3], but the free convection occurs when the negative temperature gradient in vertical direction is sufficiently great.

We take the origin at the centre of the channel, the z-axis along the vertical direction of walls. The uniform magnetic field $\vec{B}_0$ acts in the direction of x-axis.

The relevant magnetohydrodynamic equations for mass, momentum, magnetic field, energy and state are respectively:

$$\rho\left(\frac{\partial\vec{v}}{\partial t}+\vec{v}\cdot\nabla\vec{v}\right) = -\nabla p+\frac{1}{\mu_e}(\nabla\times\vec{B})\times\vec{B}+\rho\vec{g}+\mu_1\Delta\vec{v} \tag{1}$$

$$\frac{\partial\vec{B}}{\partial t} = \nabla\times(\vec{v}\times\vec{B})+\nu_m\Delta\vec{B} \tag{2}$$

$$\frac{\partial T}{\partial t}+\vec{v}\nabla T = \alpha\Delta T-\frac{1}{\rho C_p}\nabla\cdot q_R \tag{3}$$

$$\rho = \rho_0(1-\beta\Delta T) \tag{4}$$

in which $\vec{v}$ is the velocity, ρ the mass density, p the pressure, $\vec{g}(0,0,-g)$ the gravitational acceleration, μ_e the magnetic permeability, $\vec{B}$ the magnetic field intensity, μ_1 the viscosity, T temperature, ν_m the magnetic viscosity, α the thermal diffusivity, β the coefficient of thermal expansion and q_R the radiative heat flux and C_p the specific heat at the constant pressure.

We assume that the surface temperature of the walls vary along the vertical direction, the induced magnetic field and velocity have only a component in vertical direction and all physical variables expect temperature and pressure are function of x.

In the primary static state the temperature has the form [5]:

$$T = T_0 + f_1(x) + N_z \tag{5}$$

where N is the vertical gradient (a constant). The subscript zero denotes a reference point which will be specified later.

Then from (1) and (4), (5) we find succesively:

$$\rho = \rho_0[1 - \beta f_1(x) - \beta N_z] \tag{6}$$

$$\frac{dp}{dz} = -\rho_0 g[1 - \beta f_1(x) - \beta N_z] \tag{7}$$

where N(<0) is the upward temperature gradient.

Supose that the initial state is slightly perturbed with the perturbed quantities denoted by $\vec{v}'$, θ, $\vec{p}'$, $\vec{b}$. Eqs.(1)-(3) to the linear approximation [3] become:

$$\frac{\partial \vec{v}}{\partial t} = -\frac{1}{\rho_0}\nabla p' + \frac{1}{\mu_e \rho_0}(\nabla \times \vec{b}) \times \vec{B}_0 + \nu \Delta \vec{v} - \beta \theta \vec{g} \tag{8}$$

$$\frac{\partial \vec{b}}{\partial t} = \nabla \times (\vec{v} \times \vec{B}_0) + \nu_m \vec{b} \tag{9}$$

$$\frac{\partial \theta}{\partial t} = \alpha \Delta \theta - C\theta - Nv \tag{10}$$

where C is obtained taking account [4]:

$$\frac{1}{\rho C_p}\frac{\partial g_R}{\partial x} = \frac{4(T - T_0)}{\rho C_p}\int_0^\infty K_{\lambda_0}\left(\frac{de_{b\lambda}}{dT}\right)_0 d\lambda \tag{11}$$

$$C = \frac{4}{\rho C_p}\int_0^\infty K_{\lambda_0}\left(\frac{de_{b\lambda}}{dT}\right)_0 d\lambda \tag{12}$$

$$\frac{1}{\rho C_p}\frac{\partial g_R}{\partial x} = C\theta \tag{13}$$

where $k\lambda$ is the absorbtion coefficient, $e_b\lambda$ the Planck function and the subscript zero indicates that the quantities have been evaluated at the reference temperature T_0. In the equ. (10) we have neglected viscous and ohmic dissipation, the fluid does not absorb its own emitted radiation, in the case of an optically thin limit, that is, there is no self absorbtion, but the fluid does absorb radiation emitted by the boundaries.

It is posible to assume that the velocity and induced magnetic field are function of x and y and are given by:

$$\begin{cases} \vec{v} = (0,0,w(x,y,t)) \Rightarrow \nabla\cdot\vec{v} = 0 \\ \vec{b} = (0,0,b_z(x,y,t)) \rightarrow \nabla\cdot\vec{B} = 0 \end{cases} \tag{14}$$

Eqs. (8)-(10) however, reduce to:

$$\frac{\partial W}{\partial t} = \frac{B_0}{\mu_e \rho_0}\frac{db_z}{dx} + \nu\Delta w + \beta g\theta \tag{15}$$

$$\frac{\partial b_z}{\partial t} = B_0\frac{\partial W}{\partial x} + \nu_m \Delta b_z \tag{16}$$

$$\frac{\partial\theta}{\partial t} = \alpha\Delta\theta - C\theta - Nw;\ \nabla^2 = \Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \tag{17}$$

We have neglected $\frac{\partial p'}{\partial z}$ because we are not concerned by the forced convection. If we introduce the folowing nondimensional quantities

$$x^* = \frac{x}{l};\ y^* = \frac{y}{l};\ t^* = \frac{\nu t}{l^2};\ b_z^* = \frac{b_z}{B_0};\ W^* = \frac{Wl}{\alpha};$$
$$\theta^* = -\frac{\theta}{Nl};\ P_r = \frac{\nu}{\alpha};\ R = -\frac{g\beta N l^4}{\alpha\nu};\ M^2 = B_0^2 l^2 \frac{\sigma}{\rho_0 \nu};\ P_m = \frac{\nu_n}{\alpha} \tag{18}$$

Substituting these and imediately dropping bars one obtains:

$$\frac{\partial W^*}{\partial t^*} = P_m M^2 \frac{db_z^*}{dx^*} + \Delta W^* - R\theta^* \tag{19}$$

$$P_r\frac{\partial b_z^*}{\partial t^*} = \frac{\partial W^*}{\partial x^*} + P_m \Delta b_z^* \tag{20}$$

$$P_r\frac{\partial\theta^*}{\partial t^*} = \Delta\theta^* - F\theta^* + W^*;\ F = C\frac{l^2}{\alpha} \tag{21}$$

These wquations permit the separable solution:

$$W^* = U(x,y)\, e^{\lambda t}$$

$$\theta^* = \Theta(x,y)\, e^{\lambda t} \tag{22}$$

$$b_z^* = B(x,y)\,e^{\lambda t}$$

in which λ is assumed complex. The separated equations (19) to (21) then become:

$$\lambda U = P_m M^2 \frac{\partial B}{\partial x^*} + \Delta U - R\Theta \tag{23}$$

$$P_r \lambda B = P_m \Delta B + \frac{\partial U}{\partial x^*} \tag{24}$$

$$P_r \lambda \Theta = \Delta \Theta - F\Theta + U \tag{25}$$

Dunwoody [3] has shown that for $P_m > 1$ the principle of exchange of stabilities is valid, i.e. λ is real and the neutral instability is characterised by $\lambda = 0$.

In this case:

$$R\Theta = P_m M^2 \frac{\partial B}{\partial x^*} + \Delta U \tag{26}$$

$$\frac{\partial U}{\partial x^*} = -P_m \Delta B \tag{27}$$

$$U = F\Theta - \Delta\Theta \tag{28}$$

The elimination of θ and B between eqs. (26) - (28) results:

$$\nabla^6 U - F\nabla^4 U + \left[R - M^2 \frac{\partial^2}{\partial x^{*2}}\right]\nabla^2 U + FM^2 \frac{\partial^2 U}{\partial x^{*2}} = 0 \tag{29}$$

if we note $D = d/dx^*$ and the disturbance has the form:

$$U(x^*, y^*) = f(x^*)\cos(\alpha y^*) \tag{30}$$

we obtain (see appendix):

$$[D^6 - D^4(3\alpha^2 + F + M^2) + D^2(3\alpha^4 + \alpha^2(2F + M^2) + R + FM^2)]\, f$$

$$= [\alpha^4(1 + F) - R\alpha^2]\, f \tag{31}$$

We note

$$3\alpha^2 + F + M^2 = C_1$$

$$3\alpha^4 + \alpha^2(2F + M^2) + R + FM^2 = C_2 \tag{32}$$

$$\alpha^4(1 + F) - R\alpha^2 = C_3$$

and eq. (31) has the form:

$$[D^6 - C_1 D^4 + C_2 D^2]\, f = C_3 f \tag{33}$$

with the boundary condition

$$U = 0;\quad B = 0;\quad \frac{\partial \Theta}{\partial x^*} = 0 \quad \text{at} \quad x^* = \pm 1 \tag{34}$$

In virtute of (34) one has at the boundaries:

$$\nabla^2\left(\frac{\partial U}{\partial x^*}\right) = -P_m M^2\left(\frac{\partial^2 B}{\partial x^{*2}}\right) \tag{35}$$

from (26) and

$$P_m \frac{\partial^2 B}{\partial x^{*2}} = -\frac{\partial U}{\partial x^*} \tag{36}$$

from (27). Combining (35) and (36)

$$(\nabla^2 - M^2)\frac{\partial U}{\partial x^*} = 0 \tag{37}$$

The boundary condition of f(x) obtained from (34) and (37) are therefore:

$$f(\chi^*) = 0;\quad (D^2 - \alpha^2 - M^2)Df = 0 \quad \text{at} \quad \chi^* = \pm 1 \tag{38}$$

The roots of caract. equation are:

$$\begin{aligned}
r_{1,2} &= \pm\left(\frac{C_1}{3} - 2\sqrt{\frac{p}{3}}\,\mathrm{ctg}\,2\varphi\right)\\
r_{3,4} &= \pm\left[\left(\frac{C_1}{3} + \sqrt{\frac{p}{3}}\,\mathrm{ctg}\,2\varphi\right) + i\,\frac{\sqrt{p}}{\sin 2\varphi}\right]\\
r_{5,6} &= \pm\left[\left(\frac{C_1}{3} + \sqrt{\frac{p}{3}}\,\mathrm{ctg}\,2\varphi\right) - i\,\frac{\sqrt{p}}{\sin 2\varphi}\right]
\end{aligned} \tag{39}$$

where

$$\left.\begin{aligned}
p &= c_2 - \frac{c_1^3}{3}\\
q &= \frac{c_1 c_2}{3} - \frac{2c_1^3}{27} - c_3
\end{aligned}\right\}\quad \frac{q^2}{4} + \frac{p^3}{27} > 0;\ p > 0$$

$$\varphi = \mathrm{arctg}\sqrt[3]{\mathrm{tg}\frac{\gamma}{2}}$$

$$\mathrm{tg}\,\gamma = \frac{2p^3}{27q}$$

Equation (33) has the solution

$$\begin{aligned}
f(x^*) = {} & A_1 e^{a_1 x^*} + A_2 e^{-a_1 x^*} + e^{a_2 x^*}(A_3 \cos a_3 x^* + A_4 \sin a_3 x^*) + \\
& + e^{-a_2 x^*}(A_5 \cos a_3 x^* + A_6 \sin a_3 x^*)
\end{aligned} \tag{40}$$

where

$$a_1 = \frac{C_1}{3} - 2\sqrt{\frac{P}{3}}\,\mathrm{ctg}\,2\varphi$$

$$a_2 = \frac{C_1}{3} + \sqrt{\frac{P}{3}}\,\mathrm{ctg}\,2\varphi$$

$$a_3 = \sqrt{P}/\sin 2\varphi$$

Taking account of (38) we found the boundary conditions for (40):

$$f(x^*) = 0; \quad Df = 0; \quad (D^2-\alpha^2)f = M^2 \quad \text{at } x^* = \pm 1 \tag{41}$$

This is the first part of this paper. The calculus of disturbance amplitudes, the physical interpretation of symetric and antisymetric motion, the value of critical Rayleigh number and graphically results will be the subject of the second part of this paper.

APPENDIX

Appling Laplace operator to equ. (26) we find:

$$R\nabla^2\Theta = M^2\frac{\partial}{\partial x^*}(P_m\nabla^2 B) + \nabla^4 U \tag{42}$$

by (27) result:

$$-\frac{\partial^2 U}{\partial x^{*2}} = \frac{\partial}{\partial x^*}(P_m\nabla^2 B) \tag{43}$$

Combining (42) and (43)

$$\nabla^2\Theta = \frac{1}{R}\nabla^4 U - \frac{M^2}{R}\frac{\partial^2 U}{\partial x^{*2}} \tag{44}$$

Appling Laplace operator to equ. (28) result:

$$\nabla^2 U = F\nabla^2\Theta - \nabla^4\Theta \tag{45}$$

and combining with (44) we find:

$$\nabla^2 U = \frac{F}{R}\nabla^4 U - \frac{FM^2}{R}\frac{\partial^2 U}{\partial x^{*2}} - \nabla^4\Theta \tag{46}$$

with the same procedure applied on (44) and taking account of (46) we have:

$$\nabla^2 U = \left.\frac{F}{R}\nabla^4 U - \frac{FM^2}{R}\frac{\partial^2 U}{\partial x^{*2}} - \frac{1}{R}\nabla^6 U + \frac{M^2}{R}\nabla^2\frac{\partial^2 U}{\partial x^{*2}}\right|\cdot R$$

$$\nabla^6 U - F\nabla^4 U + \left[R - M^2 \frac{\partial^2}{\partial x^{*2}}\right]\nabla^2 U + FM^2 \frac{\partial^2 U}{\partial x^{*2}} = 0 \tag{47}$$

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MAGNETOGRAVITATIONAL STABILITY OF RESISTIVE ROTATING PLASMA THROUGH POROUS MEDIUM WITH THERMAL CONDUCTION AND FINITE LARMOR RADIUS

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ABSTRACT. - The purpose of this paper is to give the dispresion equation and the stability criterion for longitudinal propagation of the perturbations in the case of an infinitely extending homogenous viscous self-gravitating plasma through porous medium with finite electrical and tharmal conductivities and finite Larmor corrections.

Introduction. In this present paper the magnetogravitational stability of resistive rotating viscous plasma through a porous medium with finite electrical and thermal conductivities and finite Larmor radius corrections is studied. The problem of magnetogravitational stability of a pure cosmic plasma flowing through a porous medium has been investigated in same studies [1], [2], [3], [4], [5].

Plasma is assumed as a compresible and viscous medium in a uniform rotational motion with angular velocity $\Omega(0,0,\Omega)$ and the same time is found under the influence of uniform vertical magnetic field $\vec{Bo}(0,0,Bo)$ and under the influence of a proper gravitational field.

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Linearised perturbation equations. It is admitted that in the plasma appear small perturbations. We neglect the squares and products of the perturbations.

The linearised perturbation equations of the plasma are

$$\frac{\partial \vec{v}}{\partial t} + 2\Omega \times \vec{v} = -\frac{1}{\rho_0}\nabla(\delta \vec{P}) + \nabla\delta\phi + \nu\nabla\vec{v} + + \frac{\nu}{3}\nabla(\nabla\cdot\vec{v}) - \frac{\nu}{k_1}\vec{v} + \frac{1}{\mu_0\rho_0}\nabla\times\delta\vec{B}\times\vec{B}_0 \tag{1}$$

$$\varepsilon\frac{\partial(\delta\rho)}{\partial t} = -\rho_0\nabla\cdot\vec{v} \tag{2}$$

$$\frac{\partial(\delta\vec{B})}{\partial t} = \nabla\times(\vec{v}\times\vec{B}_0) + \nu_m\Delta(\delta\vec{B}) \tag{3}$$

$$\frac{\partial}{\partial t}\left(\delta p - V^2\delta\rho\right) = \gamma\theta\Delta\left(\delta p - V'^2\delta\rho\right) \tag{4}$$

$$\Delta(\delta\phi) = -4\pi G\delta\rho \tag{5}$$

$$\nabla\cdot\delta\vec{B} = 0, \tag{6}$$

where $\delta\vec{P}$, $\delta\phi$, $\delta\rho$; δp, $\vec{v}$, $\delta\vec{B}$ are the perturbations in pressure tensor, gravitational potential, density, pressure, velocity and magnetic field respectively; ρ_0, ν, k_1, ε, ν_m, θ, $\gamma = \frac{C_p}{C_v}$ are the density of plasma, kinematic viscosity, permeability of the porous medium, porosity, resistivity of plasma, thermal diffusivity, ratio of the two specific heats (C_p and C_v) respectively; ∇, $\Delta = \nabla^2$ are the nabla and Laplace operatorsrespectively; G is universal gravitational constant.

We take the vertical magnetic field $\vec{B}_0$ along z-axis. In this case the components P_{kl} ($k,l = 1, 2, 3$) for the perturbation pressure tensor $\delta\vec{P}$, considering the finite Larmor radius as given by Roberts and Taylor [1], are

$$\delta P_{11} = \delta P_{xx} = \delta p - \rho \nu_0\left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right), \ \delta P_{12} = \delta P_{21} = \delta P_{xy} = \delta P_{yx}$$
$$= \delta p + \rho_0 \nu_0\left(\frac{\partial u}{\partial x} - \frac{\partial v}{\partial y}\right), \delta P_{13} = \delta P_{31} = \delta P_{xz} = \delta P_{zx} = \delta p - 2\rho_0\nu_0\left(\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}\right),$$
$$\delta P_{23} = \delta P_{32} = \delta P_{yz} = \delta P_{zy} = \delta p + 2\rho_0\nu_0\left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}\right), \tag{7}$$
$$\delta P_{22} = \delta P_{yy} = \delta p + \rho_0\nu_0\left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right), \ \delta P_{33} = \delta P_{zz} = \delta p,$$

where $\rho_0 \nu_0 = kNT/4\omega_i$, $\nu_0 = r_l^2 \omega_i/4$, k, N, T, ω_i denote the Boltzmann's constant, the number of ions, number density, ion temperature and ion gyration frequency respectively; ν_0 is the gyroviscosity, r_L is the Larmor radius; $\vec{v}(u, v, w)$.

The perturbation $\delta\varphi(z,t)$ for the longitudinal propagation (paralel to the magnetic field) have the form:

$$\delta\varphi(z, t) = \varphi^* \exp(ikz + int) \tag{8}$$

where φ^* is the amplitude, k is the wave number and n (may be complex) is the frequency of the disturbance.

Using the relations

$$(\nabla \times \delta\vec{B}) \times \vec{B}_0 = B_0 \frac{\partial \delta\vec{B}}{\partial z} - B_0 \nabla(\delta B_z)$$
$$\nabla \times (\vec{v} \times \vec{B}) = B_0 \frac{\partial \vec{v}}{\partial z} - \vec{B}_0 \frac{\partial w}{\partial z}$$
$$2\vec{\Omega} \times \vec{v} = -2\Omega v \vec{\varepsilon}_x + 2\Omega u \vec{\varepsilon}_y$$
$$\nabla \cdot \delta\vec{P} = \frac{\partial}{\partial z}(\delta P_{xz})\vec{\varepsilon}_x + \frac{\partial}{\partial z}(\delta P_{yz})\vec{\varepsilon}_y,$$

where $\vec{\varepsilon}_x$, $\vec{\varepsilon}_y$ are the unit vectors, and we obtain from (1)-(5) the following algebraic equations:

$$\left[in + \nu\left(k^2 + \frac{1}{K_1}\right)\right]u^* - 2\left(\Omega - \nu_0 k^2\right)v^* - \frac{ikB_0}{\mu_0\rho_0}\delta B_x^* = 0 \tag{9}$$

$$\left[in + \nu\left(k^2 + \frac{1}{k_1}\right)\right]v^* + 2\left(\Omega - \nu_0 k^2\right)u^* - \frac{ikB_0}{\mu_0\rho_0}\delta B_y^* = 0 \tag{10}$$

$$\left[in + \nu\left(\frac{4}{3}k^2 + \frac{1}{k_1}\right)\right]w^* - ik\delta\phi^* + ik\frac{\delta p^*}{\rho_0} = 0 \tag{11}$$

$$\delta\rho^* = -\frac{k\rho_0}{n\varepsilon}w \tag{12}$$

$$\delta B_x^* = \frac{ikB_0}{\Omega_m}u^* \tag{13}$$

$$\delta B_y^* = \frac{ikB_0}{\Omega_m}v^* \tag{14}$$

$$\delta B_z^* = 0 \tag{15}$$

$$\delta p^* = \frac{(in\gamma + \Omega_k)V^2}{in + \Omega_k}\delta\rho^* \tag{16}$$

$$ik\delta\phi^* = -\frac{4\pi i G\rho_0}{n\varepsilon}w^*, \tag{17}$$

where $\Omega_k = \gamma\theta k^2$.

With the help of the relations

$$\vec{v} = \frac{\partial\xi}{\partial t} = in\xi = \omega\xi \tag{18}$$

we define the displacement vector $\xi(\xi_x, \xi_y, \xi_z)$, where $\omega = in$.

Substituting $\delta\rho$, δB_x, δB_y, $\delta\phi$, δp from (12), (13), (14), (16), (17) respectively in equations (9)-(11) we obtain:

$$\left[\omega + \nu\left(k^2 + \frac{1}{k_1}\right)\right]\xi_x - 2\left(\Omega - \nu_0 k^2\right)\xi_y + \frac{k^2V_A^2}{\Omega_m}\xi_x = 0 \tag{19}$$

$$\left[\omega + \nu\left(k^2 + \frac{1}{k_1}\right)\right]\xi_y + 2\left(\Omega - \nu_0 k^2\right)\xi_x + \frac{k^2V_A^2}{\Omega_m}\xi_y = 0 \tag{20}$$

$$\left(\omega + \Omega_k\right)\left[\omega^2 + \omega\nu\left(\frac{4}{3}k^2 + \frac{1}{k_1}\right)\right] + \frac{1}{\varepsilon}\left(J^2\omega + J'^2\Omega_k\right)\xi_z = 0\,, \tag{21}$$

where $\Omega_m = \omega + \nu_m k^2$, $J^2 = k^2V_s^2 - 4\pi G\rho_0$, $J'^2 = k^2V_s'^2 - 4\pi G\rho_0$,

where $V_s^2 = \gamma p_0/\rho_0$, $V_s'^2 = \frac{1}{\gamma}V_s^2$, $\gamma = C_p/C_v$.

By the folowing substitutions:

$$\Omega = \nu\left(k^2 + \frac{1}{k_1}\right), \ \omega_\nu = \omega + \Omega, \ \tilde{\Omega} = \nu\left(\frac{4}{3}k^2 + \frac{1}{k_1}\right), \ \tilde{\omega}_\nu = \omega + \tilde{\Omega} \tag{22}$$

$$A = 2\left(\Omega - \nu_0 k^2\right), \ B = \frac{1}{\varepsilon}\left(J^2\omega + J'^2\Omega_k\right)$$

$$\omega_k = \omega^2 + \omega\Omega_k ,$$

equations (19)-(21) can be reduced to the form:

$$\left(\Omega_m\omega_\nu + k^2V_A^2\right)\xi_x - A\Omega_m\xi_y = 0 \tag{23}$$

$$\left(\Omega_m\omega_\nu + k^2V_A^2\right)\xi_y + A\Omega_m\xi_x = 0 \tag{24}$$

$$\left(\omega_k\tilde{\omega}_\nu + B\right)\xi_z = 0 . \tag{25}$$

Dispersion equation. Equation (23)-(25) have non trivial solutions if the determinant D of the following matrix vanishes

$$\begin{pmatrix} \Omega_m\omega_\nu + k^2V_A^2 & -A\Omega_m & 0 \\ A\Omega_m & \Omega_m\omega_\nu + k^2V_A^2 & 0 \\ 0 & 0 & \omega_k\tilde{\omega}_\nu + B \end{pmatrix} \begin{pmatrix} \xi_x \\ \xi_y \\ \xi_z \end{pmatrix} = 0 ,$$

so that

$$D = \begin{vmatrix} \Omega_m\omega_\nu + k_2V_A^2 & -A\Omega_m & 0 \\ A\Omega_m & \Omega_m\omega_\nu + k^2V_A^2 & 0 \\ 0 & 0 & \omega_k\tilde{\omega}_\nu + B \end{vmatrix} = 0 .$$

We obtain the dispersion equation for the longitudinal propagation

$$\left(\omega_k\tilde{\omega}_\nu + B\right)\left[\left(\Omega_m\omega_\nu + k^2V_A^2\right)^2 + A^2\Omega_m^2\right] = 0 . \tag{28}$$

On equating the first factor of eq. (28) to zero we get

$$\omega_k \tilde{\omega}_\nu + B = 0 \tag{29}$$

and on equating the second one of eq. (28) to zero we get:

$$\left(\Omega_m \omega_\nu + k^2 V_A^2\right)^2 + A^2 \Omega_m^2 = 0\,. \tag{30}$$

We limit the discussion at the dispersion relation (29). Eq. (29) can be brought to the form:

$$\begin{aligned} &\omega^3 + \omega^2 \left[\nu\left(\frac{4}{3}k^2 + \frac{1}{k_1}\right) + \Omega_k\right] + \\ &+ \omega\left[\Omega_k \nu\left(\frac{4}{3}k^2 + \frac{1}{k_1}\right) + \frac{1}{\varepsilon}J^2\right] + \frac{1}{\varepsilon}\Omega_k J'^2 = 0\,. \end{aligned} \tag{31}$$

This is identical to Vyas', Chhajlani' [6] (cf. eq. 25).

In the absence of the thermal diffusivity ($\theta = 0$, $\Omega_k = 0$) and the porosity of medium ($\varepsilon = 1$, $k_1 = \infty$) eq. (31) is reduced to

$$\omega^2 + \omega\nu\left(\frac{4}{3}k^2\right) + J^2 = 0\,. \tag{32}$$

This is identical to Vasiu' [7] (cf. eq. 37) for ($\beta = 0$, $\nu_c = 0$).

Equation (31) is reduced to the form

$$a_0\omega^3 + a_1\omega^2 + a_2\omega + a_3 = 0 \tag{33}$$

where

$$a_0 = 1\,,\ a_1 = \nu\left(\frac{4}{3}k^2 + \frac{1}{k_1}\right) + \Omega_k$$

$$a_2 = \Omega_k \nu\left(\frac{4}{3}k^2 + \frac{1}{k_1}\right) + \frac{1}{\varepsilon}J^2$$

$$a_3 = \frac{1}{\varepsilon}\Omega_k J'^2\,.$$

According to Routh-Hurvitz's criterion for the dynamical stability of the system all the roots of the eq. (33) have negative real parts ($\mathrm{Re}(\omega) < 0$), if and only if all the principal diagonal minors Δ_i ($i = 1, 2, 3$) of Hurwitz's determinant D are positive ($\Delta_1 > 0$). The determinant D is

$$D = \begin{vmatrix} a_1 & a_3 & 0 \\ a_0 & a_2 & 0 \\ 0 & a_1 & a_3 \end{vmatrix} \tag{34}$$

and the principal diagonal minors Δ_i have the form

$$\Delta_1 = a_1 = \nu\left(\frac{4}{3}k^2 + \frac{1}{K_1}\right) + \Omega_k > 0 \tag{35}$$

$$\Delta_2 = \begin{vmatrix} a_1 & a_3 \\ 1 & a_2 \end{vmatrix} = a_1a_2 - a_3 = [\nu(\frac{4}{3}k^2 + \frac{1}{K_1}) + \Omega_k]$$
$$[\Omega_k\nu(\frac{4}{3}k^2 + \frac{1}{K_1}) + \frac{1}{\epsilon}J^2] - \frac{1}{\epsilon}\Omega_k(J')^2 > 0$$

$$\Delta_3 = \begin{vmatrix} a_1 & a_3 & 0 \\ 1 & a_2 & 0 \\ 0 & a_1 & a_3 \end{vmatrix} = a_3\begin{vmatrix} a_1 & a_3 \\ 1 & a_2 \end{vmatrix} = a_3\Delta_2 = \frac{1}{\epsilon}\Omega_k(J')^2 \cdot \Delta_2 > 0 \ .$$

Thus magnetized self-gravitating plasma with finite and thermal conductivities in porous medium is stable if

$$J'^2 > 0$$

or

$$k^2V_s'^2 - 4\pi G\rho_0 > 0 \ , \tag{36}$$

if

$$k_J'^2 = 4\pi G\rho_0/V_s'^2 \tag{37}$$

medium is stable for $k > k_J'$, where k_J' is modified Jeans'wave number for thermally conducting medium.

For nonviscous ($\nu = 0$), thermally nonconducting ($\Omega_k = 0$) selfgravitating porous medium, the dispersion equation (31) becomes

$$\omega^2 + \frac{1}{\varepsilon} J^2 = 0 . \qquad (38)$$

The condition of stability is

$$J^2 > 0 \qquad (39)$$

where $J^2 = k^2 V_s^2 - 4\pi G \rho_0$. If

$$k_y^2 = 4\pi G \rho_0 / V_s^2 , \qquad (40)$$

medium is stable for $k > k_J$, where k_J is Jeans'wave number.

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STUDIA UNIV. PABEŞ-BOLYAI, PHYSICA, XXXVII, 2, 1992

THE INDUCED BACKSCATTERING PROCESS CONSIDERED AS A FREE ELECTRON LASER

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ABSTRACT. - In a plasma that has an anisotropic electron distribution function the process of stimulated "bremsstrahlung" (backscattering) could lead to the super-radiance phenomenon, which is connected with the interaction from a free electron laser. In this paper we present an analysis of this induced emission of backscattering, which can be bigger than the absorbtion. The condition for amplification in such a process is determined and the gain factor is calculated in the classical limit of the problem.

1. Introduction. In 1962 was firstly observed that in a plasma the stimulated bremsstrahlung emission [1] can be bigger than the absorbtion. In these paper we want to analyse this proces from the point of view of the possibility that the induced backscattering could be considered as a free electron laser, in which an amplification of this radiation takes place, the frequencies of such a device being tunable. Without giving a detailed mathematical description of the backscattering process we can see that the atenuation due to this induced radiation, which may be written under a known form [2], leads to the condition for an amplification:

$$Z\left(\frac{\omega_p}{\omega}\right)^2 > \frac{2}{3}\left(\frac{v\theta}{c}\right)^3. \tag{1}$$

or

$$n\cdot Z > 4\times 10^{11}\cdot\left(\frac{h\,\omega}{k\,T}\right)^2\cdot T^{\frac{7}{2}}. \tag{2}$$

where the amplification (gain) length is given by:

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$$L = \left(\frac{c}{v\theta}\right) = 1.18 \times 10^{31} \cdot \frac{T^{3/2}}{n^2 \lambda^2} \qquad (3)$$

where v_θ is the electron thermal velocity, ω_p is the plasma frequency, ω is the radiation trequency, n-the electron density and T is the plasma temperature, $h\omega$ being the photon energy. We will analyse separately these relations, our aim being here the calculation of the gain factor Λ of the backscattering process and of the imposed conditions upon the electron distribution function. The gain factor Λ is defined in the backscattering attenuation equation [1]:

$$\frac{1}{\varepsilon} \cdot \frac{d\varepsilon}{dt} = -v \cdot \left(\frac{\omega_p}{\omega}\right)^2 \Lambda. \qquad (4)$$

Λ being a numerical quantity which depends on the electron distribution nature; $\Lambda>0$ for an isotropic distribution and $\Lambda<0$ for a sufficiently anisotropic electron distribution. A parallel process to the backscattering one is the Compton scattering in the relativistic case or the Thomson scattering in the nonrelativistic situation $v \ll c$. The Compton scattering is described by the following equation:

$$\frac{1}{\varepsilon} \cdot \frac{d\varepsilon}{dt} = -n \cdot \left(\frac{8\pi}{3}\right) \cdot \left(\frac{e^4}{m^2 c^3}\right). \qquad (5)$$

and finally, for the backscattering attenuation we have:

$$\frac{1}{\varepsilon} \cdot \frac{d\varepsilon}{dt} =- \frac{16\pi^2 n^2 Z e^6}{m^3 v_\theta^3 \omega^2} \cdot \Lambda \qquad (6)$$

where μ is the plasma collision frequency and ε is the photon energy. If we make a numerical analysis for the gain condition given by the equation (3), we see that for the following data: $n = 10^{22}$, T = 100eV, $\lambda = 0.1\mu$ we will obtain a gain length L = 1.1β cm and for $n = 10^{18}$, T = 10eV, and $\lambda = 10\ \mu$, L = 3.7 m. The conclusion is that for a valuable gain length L we need heigh densities n of the electrons.

2. The calculation of the gain factor. The problem of stimulated backscattering is essentially a quantic one, but we could work in the classical approximation, when $h\omega \ll kT$ for radiofrequency waves emission. A perturbation theory will be used. The absorbtion energy, which is of second order in radiation field E(w,k) and in the noise potential$\phi = \sum \phi(\Omega, K)$ can be written as [2]:

$$\frac{\partial \varepsilon}{\partial t} = \vec{J}^3 \vec{E} = e \cdot \int d^3 v \cdot \vec{E} \vec{v} \cdot \delta f^3 \tag{7}$$

which can be detailed under the form:

$$\frac{\partial \varepsilon}{\partial t} = i \cdot \left(\frac{e^4}{m^3} \right) \cdot \int d^3 v \vec{E} \cdot \vec{v} \cdot \int d^3 \vec{K} d\Omega \cdot \frac{\langle \phi \phi^* (\vec{K}, \Omega) \rangle}{(\omega + \vec{k} \cdot \vec{v})} \cdot \frac{\vec{k}}{(\Omega + \omega + (\vec{K} + \vec{k} \cdot \vec{v}))}$$

$$\cdot \frac{\partial}{\partial \vec{v}} \cdot \left[(\vec{e} + \vec{v} \cdot \vec{B}) \cdot \frac{\partial}{\partial \vec{v}} \cdot \frac{\vec{K}}{(\Omega + \vec{K} \cdot \vec{v})} + \vec{K} \cdot \frac{\partial}{\partial \vec{v}} \cdot \frac{(\vec{E} + \vec{v} \times \vec{B})}{(\omega + \vec{k} \cdot \vec{v})} \right] \cdot \frac{\partial f}{\partial \vec{v}} \cdot \tag{8}$$

$\vec{B}$ being the radiation selfmagnetic field. Because we select the nonrelativistic case $v \ll c$, we can neglect $\vec{K} \cdot \vec{v}$ and $\vec{B}$ and for the noise fluctuations we can use the screened static potential:

$$\langle \Omega \cdot \Omega^* \rangle = \frac{2}{\pi} \cdot \frac{n - Ze^2}{(K^2 + K_0^2)^2} \tag{9}$$

K_0 being the Debye wavenumber. After some calculations, by using in the equation (8) the dominant term in the integral $\int d^3 K \cdot d\Omega$, we have:

$$\frac{\partial \varepsilon}{\partial t} = \left(\frac{16 \pi^2 n^2 - Ze^6}{m^3 v_\theta^3 \omega^2} \right) \cdot \frac{E^2}{8\pi} \cdot \left[\frac{v_\theta^3}{\pi} \cdot \int \frac{d^3 v}{v^2} \log \left(1 + \frac{K^2 \cdot v^2}{(\omega^2 + \omega_p^2} \right) \cdot \right.$$

$$\left. \left(\frac{1}{2} (e - e(\vec{v} \cdot \vec{v})^2 \cdot \frac{\partial f_+}{\partial \vec{v}} + (e - e(\vec{v} \cdot \vec{v}) (e \cdot \vec{v}) \right] \cdot \frac{\partial f_-}{\partial \cdot \vec{v}} \tag{10}$$

If the distribution function f is sufficiently anisotropic, we can define the gain factor by comparing the equations (10) and (6):

$$A = -\frac{4\pi}{3}\cdot \log A\cdot v_\theta^3\cdot f_0(0) = -\frac{\pi}{3}\cdot\left[\log\left(1+\frac{(2kT)^2}{h^2(\omega^2+\omega_p^2)}\right)\right]\cdot v_\theta^3\cdot f_0(0) \qquad (11)$$

in the case of the attenuation of the radiation field. For an anisotropic distribution, with an axial simmetry arround an axis $\vec{a}$, f can be developed in the Legendre polynomials:

$$f = \sum_n f_n\cdot P_n(\vec{a}\cdot\vec{v}) \qquad (12)$$

and

$$\frac{\partial f}{\partial \vec{v}} = \sum_n f_n\cdot\frac{\partial P_n(\vec{a}\cdot\vec{v})}{\partial\vec{v}} \qquad (13)$$

The spherical harmonics theorem could be used with the purpose to integrate $\int d^3\vec{K}\cdot d\Omega$ and we should obtain the final form of Λ:

$$\Lambda = -\frac{4\pi}{3}\cdot\left(v_\theta^3\cdot f_o(0) + \frac{3}{5}\cdot v_\theta^3\cdot[1-3(\vec{e}\cdot\vec{a})^2]\cdot\int\frac{d\vec{v}}{v}\cdot f_2(v)\right) \qquad (14)$$

with $0\le(\vec{e}\cdot\vec{a})^2\le 1$. To have an amplification the following condition must be satisfied ($\Lambda > 0$):

$$\frac{6}{5}\cdot\int\frac{d\vec{v}}{v}\cdot f_2(v) > f_0(0)\,. \qquad (15)$$

This classical approximation for the backscattering is applied for small values of the frequency ω, but in this case that ω is near the natural resonance frequencies (ω_p, the gyrofrequency and the ion-acoustic frequency). But an anisotropic plasma is unstable and the high amplitude oscillations (instabilities) could spread the radiation. The classical condition to have an induced backscattering with a gain factor given by the equation (10) can be used for various cases, like that of an electron beam having a gaussian distribution, which propagates through the static ions of the plasma. The distribution function is in this case of the form:

$$f(v) = \frac{1}{\pi^{\frac{3}{2}} \cdot \bar{v}_\theta^3} \cdot \exp\left[-\frac{(v-v_D)^2}{v_\theta^2}\right] \tag{16}$$

and

$$f_0(0) = \frac{1}{\pi^{\frac{3}{2}}} \cdot \exp\left[-\frac{v_D^2}{v_\theta^2}\right] \tag{17}$$

By evaluating the integral $\int f_2(v) \cdot \frac{d\bar{v}}{v}$ with the special method of the "sadle Point", for big values of $\left(\frac{v_D}{v_\theta}\right)$, after a straightforward calculations, we obtain the following gain condition:

$$\frac{6}{5} \cdot \sqrt{\pi} \cdot v_D^3 > \exp\left[-\left(\frac{v_D}{v_\theta}\right)^2\right] \tag{18}$$

where $v_D < v_\theta$.

3. Conclusions. We have intended here to demonstrate the possibility of an amplification of stimulated "bremsstrahlung" (backscattering) radiation by using the classical approximation. We could make further an analysis with the aim to see that the gain is small in this case, with the exception of dense plasmas. We see that the gain depends of the plasma collision frequency too, which gives the plasma relaxation rate to the equilibrium and to an anisotropic situation. The conclusion is that the gain could be obtained easier for low frequencies radiations, but in this case we must try that our analysis remove these effects. At higher, optical frequencies the radiation gain can take place before the excitation of plasma instabilities, all the resonance frequencies being much smaller than the radiation frequency ω.

In this case we are obliged to use the quantic theory (the simplest case is the relativistic one, when $v \ll c$). Then it is necessary a more detailed quantic (and classical) analysis of the relativistic case of the obtained radiation gain process in the optical region of the basckscattering in a plasma. Some experiments, that are possible only in the laboratories where very dense and hot plasmas can be produced, could be made with the aim to verify these phenomena which we have discussed here. We have demonstrated that, for the given exemple, it is possible that the amplification take place only in the classical limit. Also an analysis which would use the particle simulation technique should be necessary for the discussed phenomenon.

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RESTRUCTURATION KINETICS IN THORIA-URANIA

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ABSTRACT. - The grain growth in the Thoria-Urania advanced nuclear fuel is considered in the frame of the atomic diffusion. The semiempirical constants deduced are reported. It appears that within a 3 μm error the model reasonably fits the the experimental data.

Introduction. The Thoria-Urania mixed oxide, $(U,Th)O_2$, is considered as a potential fuel for the Pressurised Heavy Water Reactors working as Thermal Breeders. It is a high density ceramic wich must meet additional conditions relative to the common UO_2, complying with high burn-up and reprocessing requirements [1,2]. Moreover, in order to allow a complete post-irradiation evaluation, the restructuring kinetics of the fuel must be well characterized.

Our previous studies on the atomic hemogeneity in Thoria-Urania [3,4] suggested that the mass diffusion is the dominating mechanism in the formation of the solid solution. Therefore, a diffusion model is assumed now in a numerical analysis of the grain growth kinetics of Thoria-Urania. Fortunately, by contrast to $(U,Pu)O_2$, [6] the high chemical stability of Thoria avoids an alteration of the metal/oxygen ratio.

Theory. If mass diffusion is assumed, the fraction of grains which will grow, dF, is given by [7]:

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$$\frac{dF}{dt} = -\lambda_0 \ \exp\left[-\frac{Q}{RT}\right] \tag{1}$$

which yields for isothermal annealing:

$$F = F_0 \ \exp\left[-\lambda_0 \exp\left(-\frac{Q}{RT}\right)\right] \tag{2}$$

where F_0 is the initial fraction of unrecrystallized grains, Q is the activation energy and λ_0 is a constant. Eq. (1) may be integrated for temperature transients also [7], without additional physical constants to be considered. In order to find the λ_0 and Q constants, eq. (2) is transformed for grain sizes as:

$$\frac{D_\infty - D}{D_\infty} = A \exp\left[-\lambda \, t \exp\left(-\frac{Q}{RT}\right)\right] \tag{3}$$

where D_∞ is taken as an asymptotic limiting value of the grain size specific only for this type of fuel [5].

For an isothermal annealing one obtains:

$$D = D_\infty \{1 - A \exp \left[C(t) * t\right]\} \tag{4}$$

which may be conveniently used to fit the experimental data by the least squares procedure.

Experimental. The pellets used for the out of reactor modelling of the grain growth were prepared by a conventional powder mixing, pressing and sintering in an optimized procedure [5]. The density, homogeneity and pore size distribution were controlled to fit the in-reactor requirements.

The annealing was performed in dry hydrogen for times ranging up to 300 hours at 1873, 1973, 2073 and 1173°K. Five specimens were analysed for every annealing temperature.

The grain size was measured by the linear intercept method by using Scanning Electron Microscopy micrographs.

Numerical procedure. Since the parameters of the sintered ceramics are usually affected by a large spread, when applying the least squares procedure precautions should be taken to avoid local minimums or saddle points. Therefore, three numerical procedures were considered in parallel in order to avoid erroneous fits: a Monte-Carlo search, the conjugate gradient algorithm and a quasi Newton algorithm. For the second and third procedures the IMSL ZCGR and ZXMIN [8] procedures were used on a 64 bit machine.

Results and discussions. The comparison of the parameters obtained by the three methods were very close, eliminating the hypothesis of local minimums. Thus, we obtained the following temperature dependences of the parameters in model (4):

$$D_{\infty}(T) = -30,685 + 0,03737 * T \pm 3 \qquad (5)$$

where T is the absolute temperature and D is measured in microns.

$$\ln [C(T)] = 25,815 - \frac{55512,6 \pm 6724}{T} \qquad (6)$$

yielding for the activation energy, Q, a value of 461.5 KJ/mol.

The constant A is affected by a quite large error,

$$A = 0,4102 \pm 0,08 \qquad (7)$$

but if a linear dependence on T is allowed,

$$A = -0,918 + 6,67*10^{-4}*T \pm 0,02 \qquad (8)$$

the error decreases at 5% which is inferior to the spread of the results for the individual measurements at a given temperature.

By using these fitted parameters, the error made in the

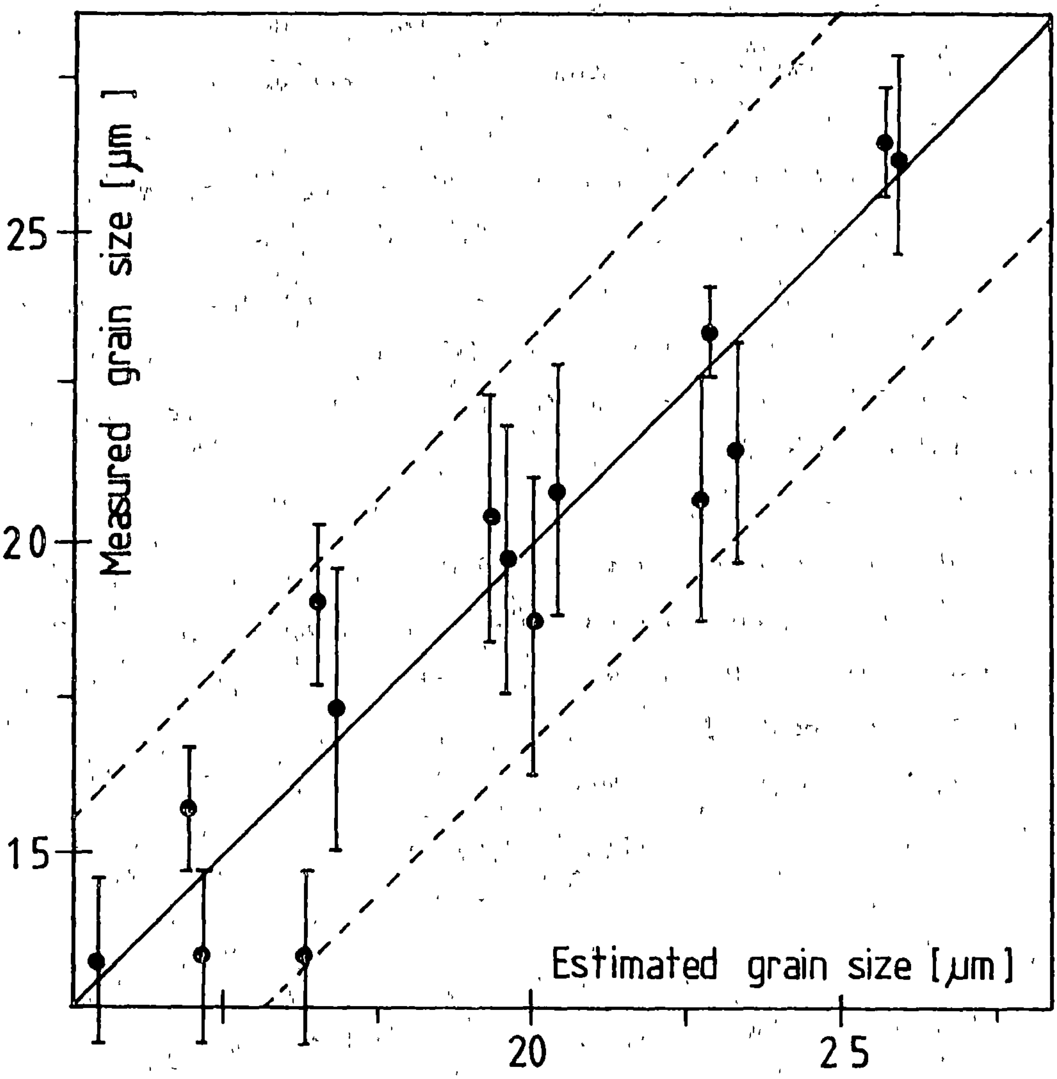

Fig. 1. The measured versus evaluated grain size according to model eq. (5)-(8). The error bars were calculated as standard deviations of the measured data.

evaluation of the grain size in given temperature and time conditions remains below 3 microns (fig. 1) which appears very reasonable for the post-irradiation evaluation of the restructuring process in an assumed irradiation history.

Although the asymptotic grain size limit was observed in all the isothermal experiments, one must observe that D_∞ and A did not appear to be constants versus temperature, a fact which induces a slight semiempirical character to the model (4). This is mainly due to the small activation energy Q which allows the grains to grow even at temperatures smaller than the plateau value. This feature was not apriori considered in the model, i.e. the initial grain size is not explicitely included.

Although the fitted parameters, eq. (5)-(8) appear to be sufficient for practical purposes, the accuracy of the theoretical model (4) could be further improved by considering the pore coalescence. This subject will be approached in a further paper.

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CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF TWO NITRONYL NITROXIDE BIRADICALS

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Received:

ABSTRACT. - The crystal structure and the magnetic properties of two nitronyl-nitroxide biradicals, NITPh(4-NIT)=1,4-bis(4',4',5',5'-tetramethyl-4,5-dihydro-1H-imidazol-2'-yl-1'-oxyl-3'-oxide) benzene (I) and NITPh(3-NIT)=1,3-bis(4',4',5',5'-tetramethyl-4,5-dihydro-1H-imidazol-2-yl-1'-oxyl-3'-oxide) benzene (II) are reported. The compounds crystallize in the monoclinic space groups: (I) $P2_1/c$ with a=6.266(1)Å, b=11.790(3)Å, c=13.781(4)Å, β=104.72(2)° and Z=2; (II) $P2_1/n$ with a=7.318(2)Å, b=25.368(3)Å, c=11.669(2)Å, β=104.72(2)° and Z=4. The magnetic susceptibilities and the room temperature EPR spectra of the free biradicals indicate that the two spins in biradical (I) are antiferomagnetically coupled with $J=-72.3$ cm^{-1}, while they are essentially not coupled in biradical (II).

Introduction. Several approaches are followed to synthesize magnetic molecular materials [1], which can be classed in inorganic [2], organic-inorganic [3], organic [4], and organic-organometallic [5], according to the chemical nature of the magnetic centers. So far Gatteschi et al. [6,7] have used nitronyl nitroxides 2-R-4',4',5',5',-tetramethyl-4,5-dihydro-1H-imidazoline-1'-oxyl-3'-oxide, NITR, as paramagnetic ligands fowards transition metal and lanthanide ions [6,7], and obtained a large number of different types of molecular based magnetic materials.

In order to obtain further information concerning to the molecular structure and magnetic properties of some molecular materials, we have investigated the NITPh(4-NIT) and NITPh(3-NIT)

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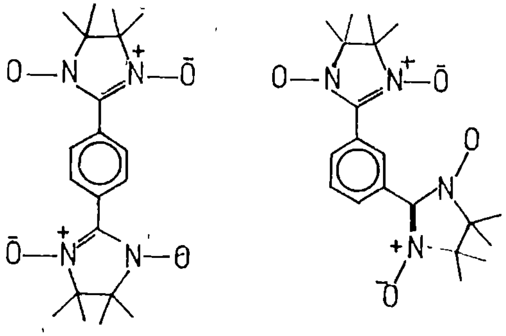
biradicals (Fig.1) by X-ray, EPR and magnetic susceptibility measurements.



I

II

Fig.1. Sketchs of NITPh(4-NIT) (I) and NITPh(3-NIT) (II) biradicals.

Experimental. The studied nitronyl nitroxide biradicals were prepared by a previously reported method [8], with minor modifications.

X-ray data were collected on an Euraf-Nonius CAD-4 four circle diffractometer using Mo-K_α radiation. The crystal structures of (I) and (II) biradicals were solved by direct methods using the program SIR [9] and Fourier methods with the SHELX-76 package [10].

Magnetic susceptibiity of (I) was measured in a field of 1.35T by using an Aztec DMS 5 Faraday balance magnetometer equipped with a Bruker B-E15 electromagnet and an Oxford Instruments CF1200S continuous flow cryostat. Magnetic susceptibilities of biradical (II) was measured in the temperature range 2.4-300 K in a field of 2T by using a Metronique Ingeniere MS03 SQUID magnetometer. Diamagnetic corrections were estimated from Pascal's constants. Single crystal EPR spectra were obtained with a Varian E9 spectrometer at X band frequency. The low temperature spectra were recordered by using an Oxford Instruments ESR9 liquid helium continuous flow cryostat. Single crystals were oriented with a CAD 4 diffractometer.

Results and discussion. A) NITPh (4-NIT).

Crystal Structure. The asymmetric unit of biradical (I) contains half atoms from the atoms corresponding to the molecular formula $C_{20}H_{28}N_4O_4$ because a symmetry center is presented in the middle of the benzen ring. The whole molecule is shwon in Figure 2.

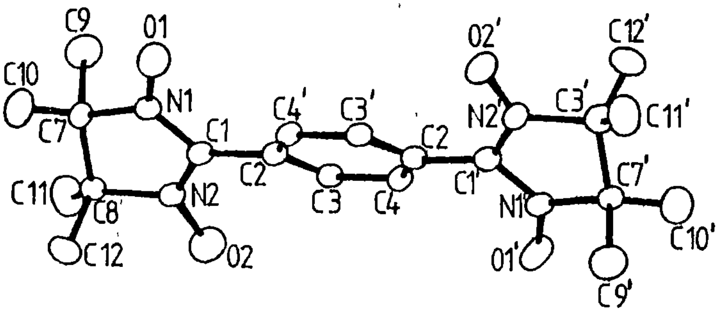


Fig.2. ORTEP view of NITPh (4-NIT).

The O1-N1-C1-N2-O2 atoms are co-planar as expected due to orbital conjugation, while the five membered heterocyclic ring is not planar, the tetramethylethylene moiety being twisted out of the plane by 0.157(4) and 0.259(4) Å. The methyl groups are staggered one relative to the other in order to relieve steric repulsion. The plane of the benzen ring makes an angle of 28.0(3)° with the radical conjugation planes, and this value ring is similar to that reported for the nitronyl nitroxide radicals NITPh [11]. The shortest intermolecular distances the NO groups are 4.670(5) Å, between the N1 and O2 atoms of molecules reported by translation in the a direction.

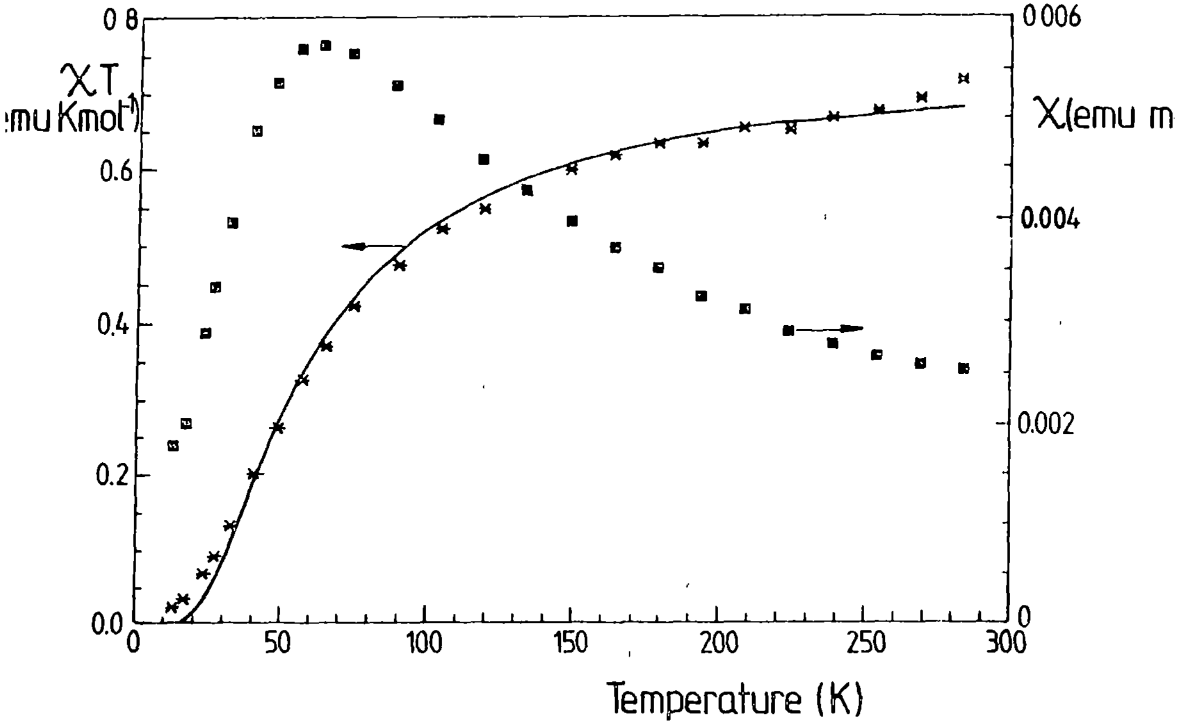


Fig.3. Temperature dependence of χ(▫) and χT(*) for NITPh(4-NIT). The solid line represents the calculated values with the best fit parameters.

Magnetic and EPR data. Figure 3 shows plots of χ and χT vs T for the biradical (I). The high χT value (≈0.7 emu K mol^{-1} at 270 K) is lower than that expected for two S=½ uncorrelated spins (χT=0.75 emu K mol^{-1}). χT curve decreases steadily with decreases of the temperature. The susceptibility gets through a maximum at T≈65 K. This behavior can be easily reproduced considering that the two S=½ spins of the biradical are antiferomagnetically coupled. The J value ($H = J\vec{S}_1 \times \vec{S}_2$) can be derived from the relation $J/k_BT_{max} = 8/5$. [12]. The value so obtained is J = -72.3 cm^{-1}, in good agreement with the value derived from the fitting of the experimental χT vs T data ($J=72.0\ cm^{-1}$) with $g=2.01$ and $R=3.3\ 10^{-2}$ where

$$R = \left[\sum (\chi T_{calc} - \chi T_{exp})^2 / \sum (\chi T_{exp})^2\right]^{1/2} \qquad (2)$$

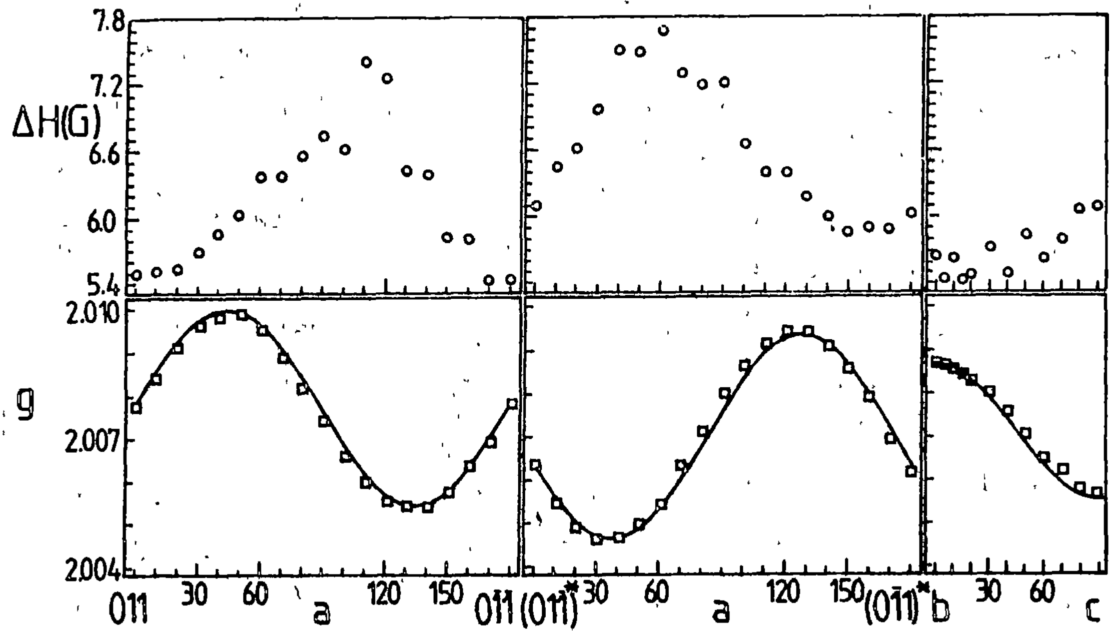


Fig.4. Angular dependence of the observed g(□) and line widths(○) values for NITPh(4-NIT) at the room temperature. The solid lines represent the best fit calculated values.

Room temperature single crystal EPR spectra of NITPh(4-NIT), recorded by rotating the crystal around the three perpendicular x, y and z axes, where x=a and y=[011], show a single exchange narrowed lorentzian line. The angular dependences of the g values and of the line width are given in Figure 4. The components of the g tensor were obtained with a standard fitting procedure [13]. The results (g_1=2.003, g_2=2.008, g_3=2.010) are in good agreement with the data reported for nitroxide and nitronyl-nitroxide radicals [14-16].

The observed values are crystal values, i.e. they corespond to the average response of the magnetically non-equivalent biradicals present in the monoclinic unit cell. It is well know that in nitroxides the lowest g value is observed perpendicular to the conjugation plane [17], therefore we considered these directions for the various magnetically nonequivalent NO groups present in the unit cell and averaged them. The result is that g_1 is expected to lie in the ac plane, along of the a direction which is in agreement with that found within experimental error.

The observed line widths are in the range of 5.4-7.8 G. Since the lines are exchange narrowed it is possible to relate the peak to peak line widths ΔH to the second moment M_2 and to the exchange interactions [18]. In principale there are three factors wich can influence the second moment: the dipolar interaction, the unresolved hyperfine splitting and the g anisotropy. We estimated these three contributions to the second moment of the line. The dipolar contribution to M_2, due the interaction between two spins of magnetically non-equivalent biradicals prevails the other broadening mechanisms. The observed ΔH can be reproduced with the usual formula for exchange coupled sysyems, $\Delta H \approx M_2/J'$ [18], with the inter-radical exange coupling constant, J', of about 0.4 cm^{-1}. This small value found for the inter-molecular coupling constant J', compared with the intra-molecular coupling constant J, confirms the goodness of the magnetic data fitting for NITPh(4-NIT)>

B) NITPh(3-NIT)

Crystal Structure. The structure of biradical (II) is characterized by the disorder existing in one of the five-membered hetero-cyclic rings. Some atoms occupy two different positions, as shwon in Figure 5, which sketches the part of the molecule where disorder is present. The atoms labeled with B have final occupation factors of 0.45(1). However, the carbon atom C19 has an occupation factor 1 because it belongs in the same time to the equatorial methyl carbon atom of the C19-C16-C20 group and to the equatorial methyl carbon atom of the C19-C16B-C20B group. The differences of bond lengths and angles are similar to those reported for other free nitronyl-nitroxide radicals [11].

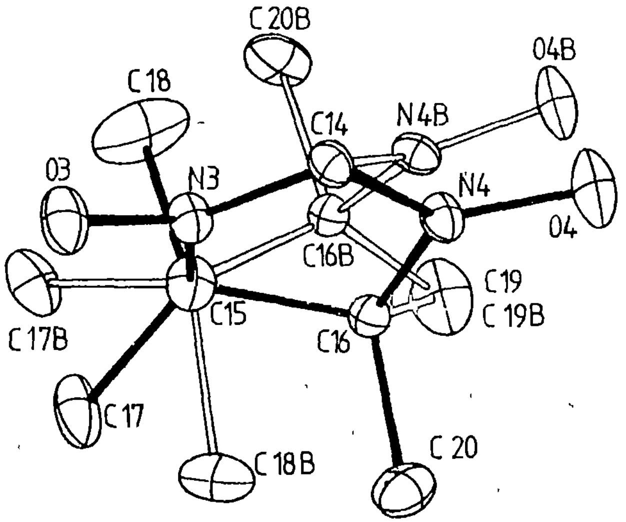


Fig.5. ORTEP view of the part of NITPh(3-NIT) displaying disorder.

Figure 6 shows the asymmetric unit, where only the B labeled atoms are shown. The fragment O1-N1-C7-N2-O2 is nearly planar; the leastsquares plane defined by these atoms shows a maximum deviation of 0.038(4) Å. The fragments O3-N3-C14-N4-O4 and O3-N3-C14-N4B-O4B (Fig. 5) show larger deviations from planarity (≈0.20(1)Å).

The plane of the benzene ring makes angles of about 35° with the

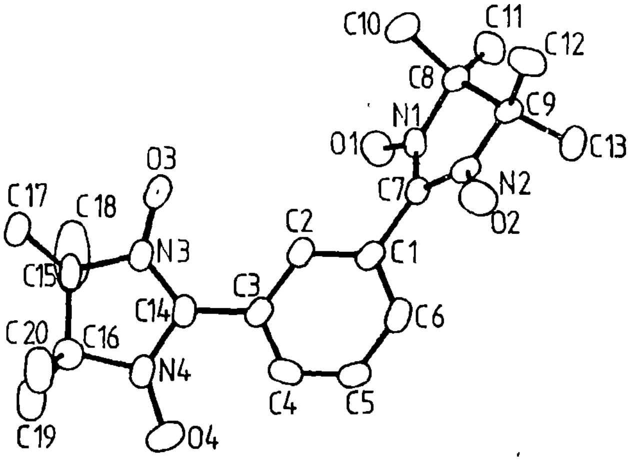


Fig.6.ORTEP view of NITPh(3-NIT)

O1-N1-C7-N2-O2 plane, 31° with the O3-N3-C14-N4-O4 plane and 36° with the O3-N3-C14-N4B plane (fig. 5). The shortest intermolecular contacts between NO groups involve nitronyl nitroxides reported by inversion center. The distances N1-O1'and O1-N1' are 3.480(5) Å, while N1-N1' and O1-O1' are 3.892(5) and 3.518(5) Å respectively; the distance O1-N2' and the symmetric one N2-O1' are longer (4.087(5) Å). Contacts between NO groups of molecules related by a translation along of the a axis, are slightly longer (O1-O2" = 4.331(5) Å and N1-O2" = 4.589(5) Å).

Magnetic and EPR data. Figure 7 shows the temperature dependence of χT for NITPh(3-NIT) which is approximately constant over 35 K, with a value of 0.72 emu KmOl^{-1}. χT decreases below this temperature at 0.495 emu Kmol^{-1} for T=2.4 K with a characteristic slope of an antiferromagnetic coupling.

Room temperature single crystal EPR specra of NITPh(3-NIT) were recorded by rotating the crystal around the b, c and $a^* = b \times c$ axes. Figure 8 shows the angular dependence of q and of the linewidth. The calculated g tensor components are: g_1=2.005,

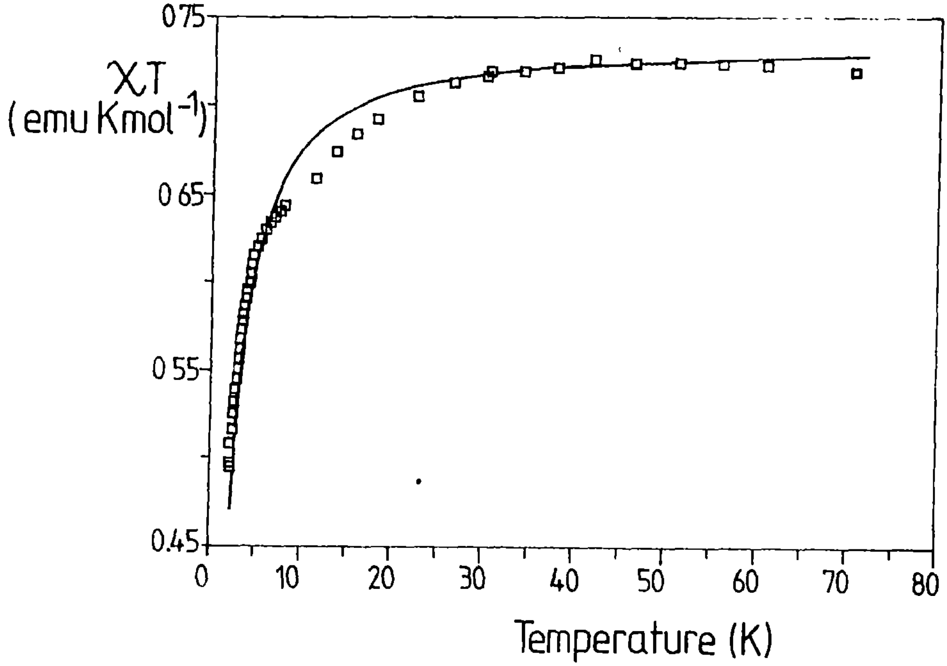


Fig.7. Temperature dependence of χT(□) for NITPh(3-NIT). The solid line represent the calculated values with the following parameters: $J=0.0 cm^{-1}$, $J'=-4.0 cm^{-1}$ and $g=1.98$.

$g_2=2.009$ and $g_3=2.010$. By the same procedure outlined for biradical (I) we found that g_1 is expected to be parallel to b axis.

The interpretation of the magnetic data requires the consideration of the coupling between the two spins as well as that between the two spins as well as that between the two NO groups related by the inversion center, represented by the coupling constants J and J', respectively. In fact it has been shown that the extend of the coupling between neighboring NO groups can be related to the geometric parameters α and d sketched in Fig. 9 and β, the angle between the normal lines to the conju-gation planes and the plane containing the four atoms [6]. In biradical

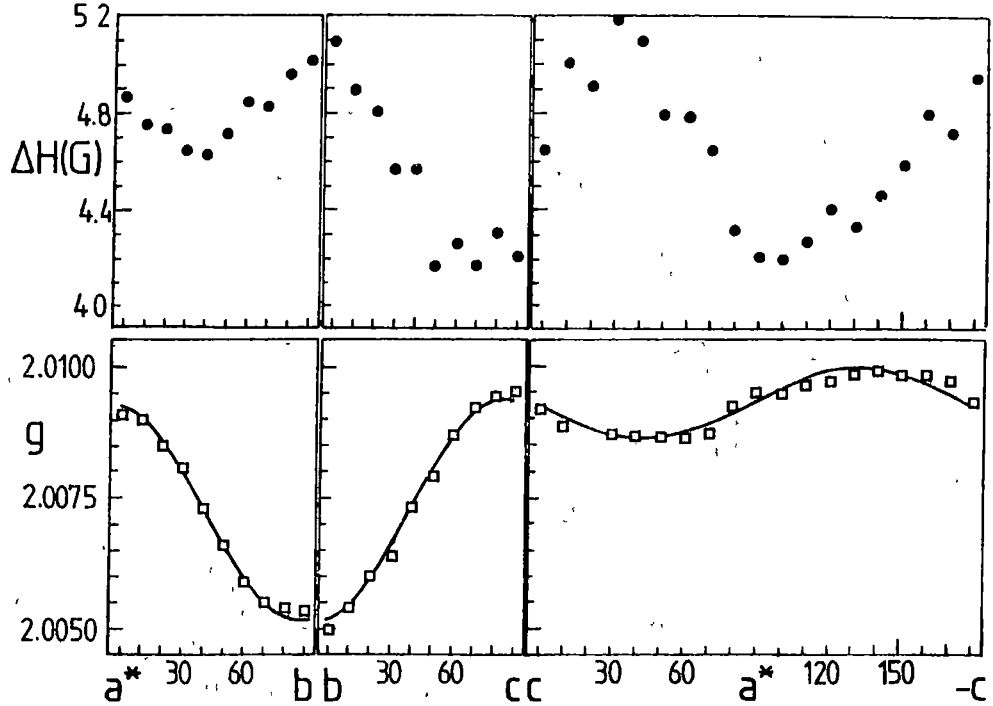


Fig.8. Angular dependence of the observed g(□) and line widths (·) values for NITPh(3-NIT) at the room temperature. The solid lines represent the best fit calculated values.

(II) we found: d = 3.48 Å, α = 98.9° and β = 67.0°. The comparison with previously reported cases [6] suggests an antiferomagnetic coupling constant J′ of about -5 cm^{-1}. Other intermolecular interactions, leading to an extendend magnetic structure, are expected to be of minor extent, and will be neglected in a first approach.

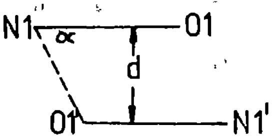


Fig.9. Geometrical relevant parameters for the magnetic interaction between two NO groups related by inversion center.

In view of these consideration the system can be considered as a system of four S=½ spins described by the following spin Hamiltonian:

$$\hat{H} = J(\vec{S}_1 \times \vec{S}_2 \times \vec{S}_3 \times \vec{S}_4) + J'\vec{S}_2 \times \vec{S}_3 \qquad (3)$$

where $(\vec{S}_1,\vec{S}_2)$ and $(\vec{S}_3,\vec{S}_4)$ are pairs of interacting spins within each biradical. The fitting procedure does not give unique results because several sets of the three parameters g, J and J′ reproduce equally well the experimental χT vs T data. Two limit cases have been considered, in which either J or J′ are set to zero. The two fits yielded respectively: i) $J=0.0$ cm^{-1}; $J'=-4.0$ cm^{-1}, $g=1.980$ and $R=1.8\times10^{-2}$ or ii) $J=-1.8$ cm^{-1}, $J'=0.0$ cm^{-1}, $g=1.975$ and $R=2.5\times10^{-2}$.

Additional information on the values of the coupling constants can be derived from the analysis of the EPR line widths, which are in the range 4.2-5.2 G. The second moment M_2 of the line must be due to the dipolar interaction, the other broadening mechanisms being at least 200 times smaller. The observed line widths can be reproduced by assuming the inter-radical J′ coupling constant of about 3 cm^{-1}. This agrees were closely with fit (i) of the magnetic data given above.

Conclusions. The analysis of the magnetic interactions confirms the fundamental importance of topology in determining the value of the exchange coupling constants J. In fact when the two nitronyl-nitroxide moieties are in the **para** position of the benzene ring, as in NITPH(4-NIT), the coupling constants are antiferromagnetic, $J=-72.3$ cm^{-1}, while in the case of the **meta** geometry of NITPh(3-NIT) spins are essentially not interacting ($J\approx0$ cm^{-1}).

The Extended Hückel approximation was used in evaluating the interaction between the SOMO's of the two NITR moieties of the radicals. With an extention of the treatement used for the weakly coupled dinuclear metal complexes the observed coupling constant mat be associated with the splitting of the two interacting SOMO's [19]. Two copper(II) complexes of the above mentioned biradicals have been investigated, too [20].

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IR STUDIES OF SOME COPPER (II) COMPLEXES WITH ANTIINFLAMMATORY DRUGS

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ABSTRACT. - In order to obtain further information on the structure of metal complexes with antiinflammatory drugs the following Cu(II) compounds: $[Cu(II)_2(aspirinate)_4](H_2O)_2$, $[Cu(II)_2(indomethacin)_4](H_2O)_2$, $[Cu(II)(ibuprofen)_2](H_2O)_2$ and $[Cu(II)(piroxicam)_2](DMF)_2$ were prepared and investigated by IR spectroscopy. The assignment of the main absorption bands from the spectra of complexes was made. The shifts of some bands and the appearance of the other new bands in the complex spectra, were explained by the participation of some structural groups to the coordination.

1. Introduction. Inflammation is an important response to tissue injury due to any cause. The importance of this multifaceted process is appreciated as the beginning of the tissue repair process, which is required to reestablish normal function [1].

Many antiinflammatory agents have been developed to inhibit some component of the inflammatory process without correcting the cause of the disease or promoting tissue repair. It has been demonstrated that copper complexes promote tissue repair processes [1]. The hypothesis that copper compounds might be active as antiinflammatory agents is supported by the finding that copper complexes are effective against arthritic and other

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degenerative diseases of man. Moreover, iy is well known that non steroidal antiinflammatory agents posses analgesic activity [2]. It is also known that a number of copper (II) coordination complexes of non steroidal antiinflammatory drugs have been shown to be more effective antiinflammatory agents than their parent drugs [1-4]. Knowing these qualities, some IR and EPR studies were reported on these complexes in order to estimate the action of the presence of transition metal ions on the local structure [5-8].

For obtaining further information on the local structure of some metal complexes with antiinflammatory drugs the copper (II) complexes with aspirinate, indomethacin, ibuprofen, and piroxicam ligands were prepared and investigated by IR spectroscopy.

2. Experimental. **$[Cu(II)_2(aspirinate)_4](H_2O)_2$.** An amount of 0.11 mols of acetylsalicylic acid was dissolved in 50 ml of ethanol and 0.2 mols of $CuSO_4$ were also dissolved in 100 ml of water. These two solutions were mixed and stirred for about 1 hour and then an amount of 200 ml of water was added to the above solu-tion. The greenish precipitate obtained was dried in air at room temperature. The structure of this compound is shown in Fig.1.

$[Cu(II)_2(indomethacin)_4](H_2O)_2$. Indomethacin (0.05 mols) was dissolved in 50 ml of ethanol. A $CuSO_4$ solution prepared by adding 0.01 mols of $CuSO_4$ to 25 ml of ethanol-water mixture (1:1), was added to the first solution. This admixture was refluxed for 0.5 hour and then mixed with 300 ml of water. The green precipitate was filtered and washed with water. Finally it was dried in air at room temperature.

[Cu(II)(ibuprofen)$_2$](H$_2$O)$_2$. This complex was prepared by the above exposed method for indomethacin compound.

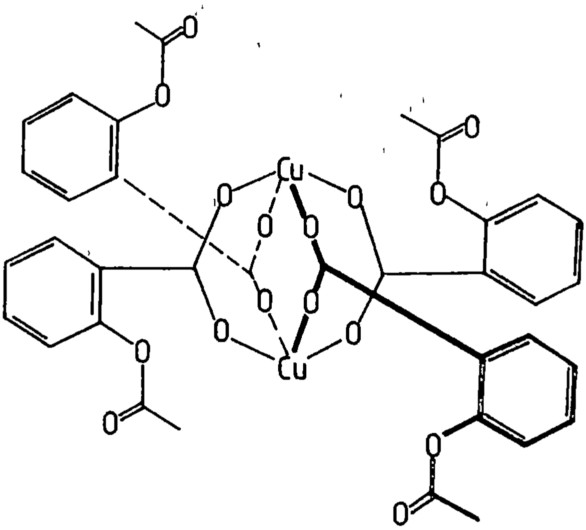

Fig.1. Dimeric structure of [Cu$_2$(aspirinate)$_4$] compound

[Cu(II)(piroxicam)$_2$] (DMF)$_2$. The Cu(II) piroxicam compound was prepared according to the following procedure: 0.11 mols of piroxicam were dissolved in 100 ml of dimethylformamide (DMF). A CuSO$_4$ solution, prepared by adding 0.05 mols of CuSO$_4$ to 100 ml of ethanol-water mixture (1:1), was added to the first solution. This mixture was refluxed under stirring for about 0.5 hour at 60°C. The greenish solid compound was filtered, washed with

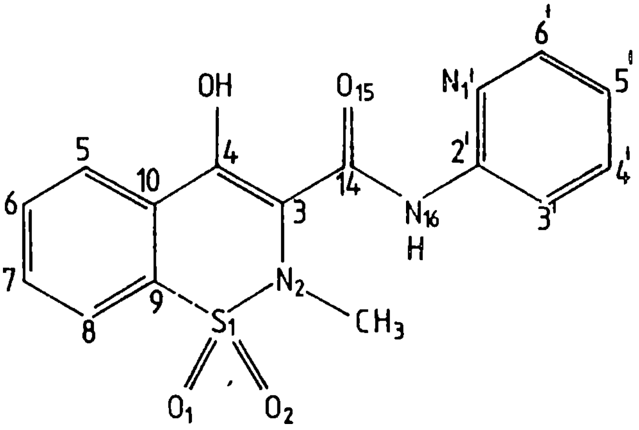

Fig.2. The structure of piroxicam

methanol and then dried in air at room temperature. The piroxicam molecular structure is shown in Fig.2.

IR absorption spectra in the range 400 to 3600 cm^{-1} were recorded in KBr pellets form on Carl Zeiss Jena spectrophotometer (UR 20 model).

3. Results and discussion. **$[Cu(II)_2(aspirinate)_4](H_2O)_2$.** Characteristic IR spectra are shown in Fig. 3. The bands observed at 1720 cm^{-1} and 1760 cm^{-1} in the free ligand spectrum may be assigned to stretching vibrations of the carbonyl groups of aspirin. Both bands are strongly diminished in intensity in the copper(II) complex spectrum and the first band is shifted to 1590

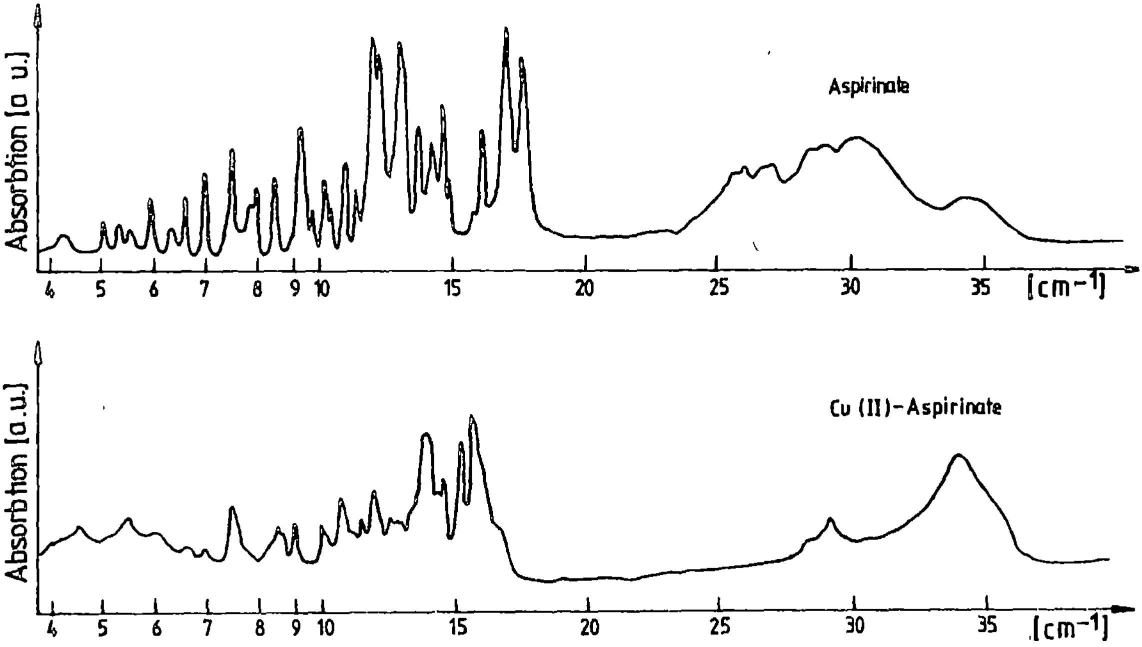

Fig.3. IR spectra of Cu(II)-Aspirinate

cm^{-1}. This fact indicates the involving of the carbonyl group in the metal cation.

The antisymmetric carboxylate stretching vibration is also shifted from 1610 cm^{-1} to 1550 cm^{-1} in Cu(II)-complex which indicates the involving of this group in coordination, too.

The band observed at 435 cm^{-1} which do not appears in the free ligand, may be attributed to the Cu-O stretching vibration. The IR spectrum of CU(II) aspirinate complex shows also an absorption band at 770 cm^{-1} which is characteristic to $\nu_{Cu-O}+\delta_{O-C=O}$ vibration. The band from 3420 cm^{-1} is due to the O-H stretching vibration of the coordination water molecules.

[Cu(II)$_2$(indomethacin)$_4$](H$_2$O)$_2$. The bands observed at 1700 cm^{-1}

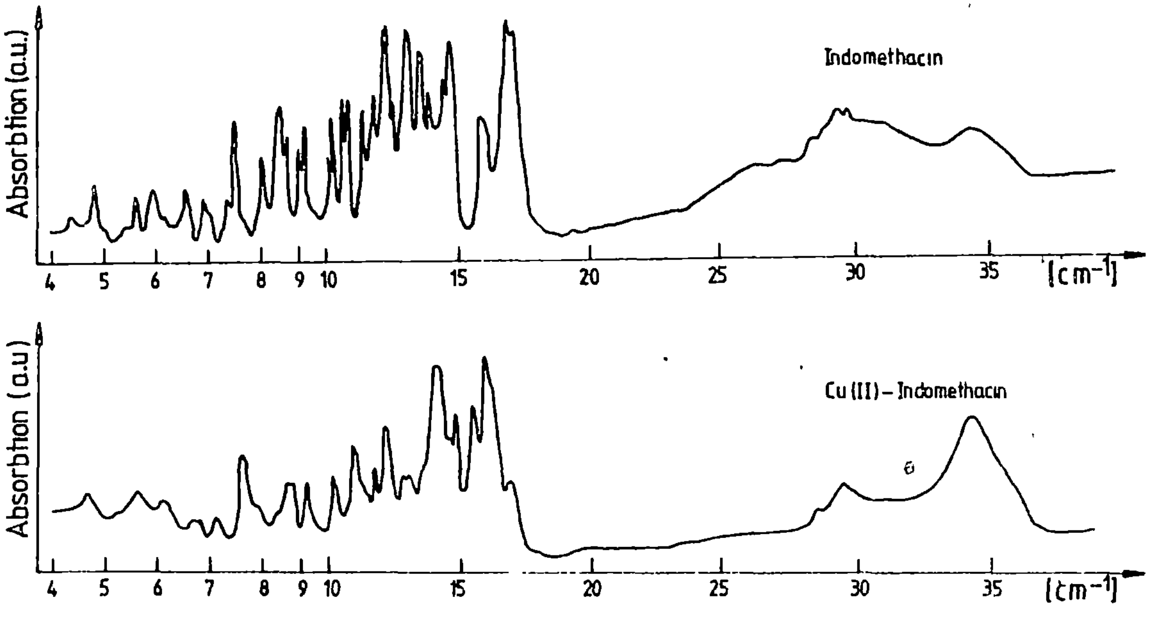

Fig.4. IR spectra of Cu(II)-Indomethacin

and 1725 cm^{-1} in the free ligand (Fig. 4) are assigned to the carbonyl groups. These bands are found in the spectrum of the metal complex at 1590 cm^{-1} and 1700 cm^{-1}, respectively. The carboxylate stretching vibration is also shifted from 1600 cm^{-1} to 1550 cm^{-1}.

We can advance the hypothesis that in the crystalline state this compound presents two kinds of dimeric species: one due to the coordination of carboxyl group, following the $Cu(II)_2(aspirinate)_4$ structure in which the Cu-Cu distance is short (≈2.7Å)[8], and the other type, using the carbonyl group for coordination, in which the Cu-Cu distance is bigger than in the first case.

The two crystallization forms named β-I and γ-I may be identified by studying the ν_{as} (COO^-) frequencies. It is important to identify the γ-I form which is more efficient antiinflammatory agent than β-I form [9].

The IR spectrum of Cu(II)-indomethacin complex shows also an absorption band at 3450 cm^{-1} due to the O-H stretching vibration of the ligand water molecules.

$[Cu(II)(ibuprofen)_2](H_2O)_2$. The frequencies observed in the 2800÷3000 cm^{-1} region, centred on 2875 cm^{-1}, 2930 cm^{-1} and 2965 cm^{-1}, are due to the methyl and to the methylene groups, in the free ligand (Fig.5).

These bands appear at the same frequencies in the Cu(II) complex. The band observed at 1730 cm^{-1} is assigned to the ν_{co} vibration of the acid group. This band appears at 1590 cm^{-1} in

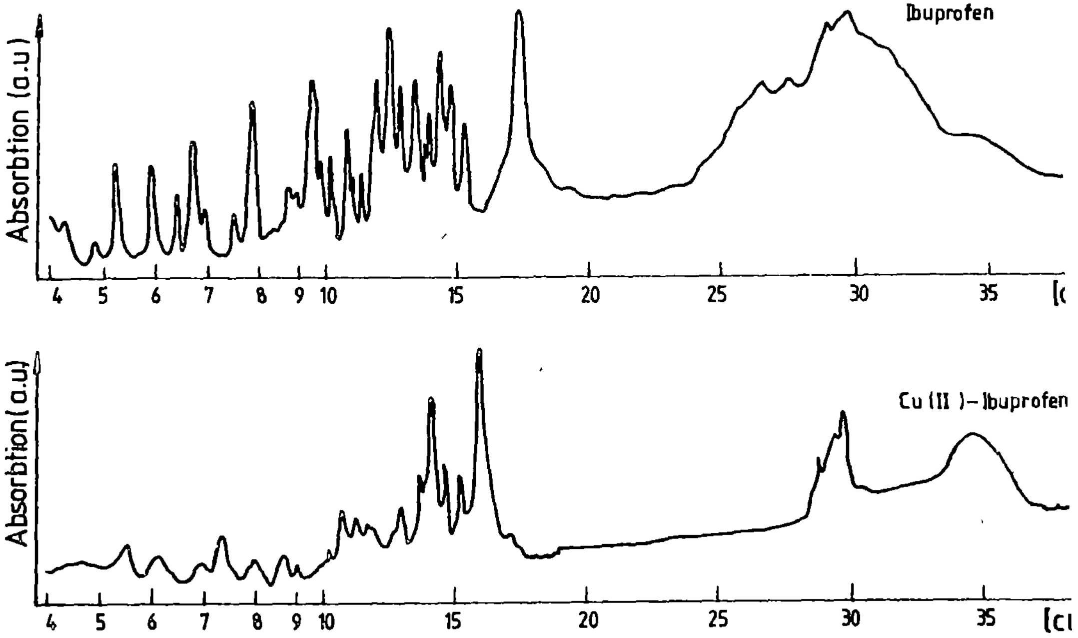

Fig.5. IR spectra of Cu(II)-Ibuprofen

the spectrum of the Cu(II)-complex. The appreciable shift in energy suggests that the COO^- group is very sensitive to complexation.

The combination bands, $\nu_{M-O}+\delta_{O-C=O}$ and $\nu_{M-O}+\nu_{C-C}$, appear at 735 cm^{-1} and 555 cm^{-1}, respectively. Cu-ligand and the $Cu-OH_2$ vibrations appear at 430+470 cm^{-1} and 530 cm^{-1}, respectively.

The 3450 cm^{-1} absorbtion band is due to the O-H stretching vibration of the ligand water molecules.

[Cu(II)(piroxicam)$_2$](DMF)$_2$. The amide I band (C=O stretching vibration) is moved from 1630 cm^{-1} to about 1600 cm^{-1} by complexation with Cu(II), in agreement with the results of the X-ray structure analysis, which shows strong metal coordination to the amide oxygen atom [10]. The sharp and strong band at 3350 cm^{-1} due to the O-H group of the free ligand is not detectable in the metal complex because of the deprotonation of the enolate O-H group [10]. However the band at 1350 cm^{-1} attribuable to the $>SO_2$ asymmetric streching vibration indicates a shift of ≈ 30 cm^{-1} upon complexation though the $>SO_2$ group does not interact with the metal ion.

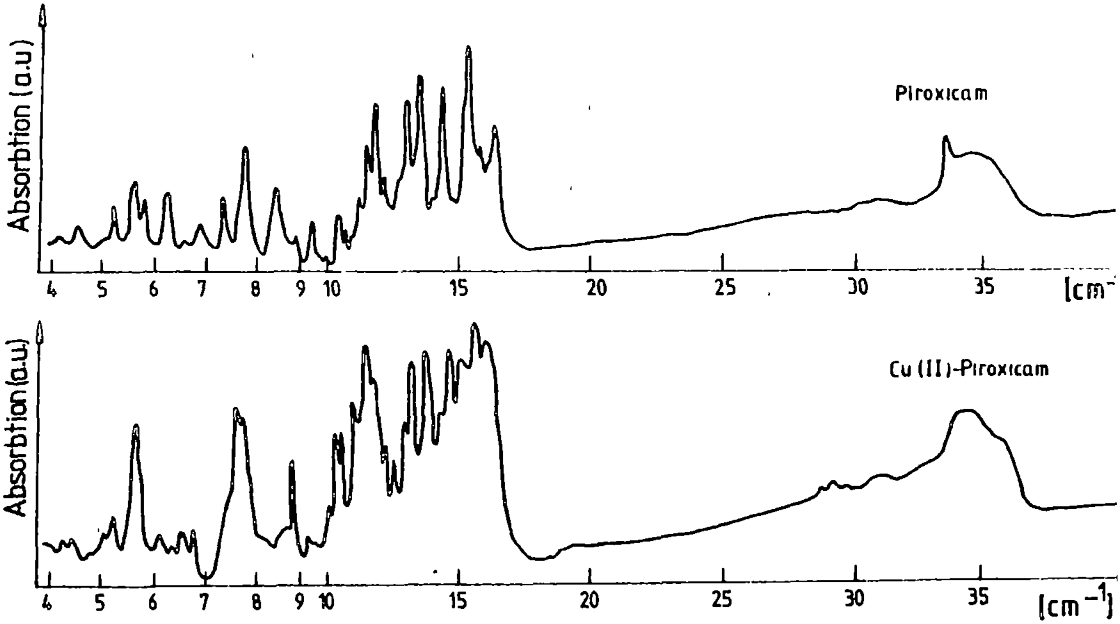

Fig.6. IR spectra of Cu(II)-Piroxicam

X-ray diffraction studies of some piroxicam metal complexes have indicated that metal ion is six-coordinated through carbonyl oxygen atom (O15) of the amido group and pyridil nitrogen atom (N1′) of the ligand molecules (Fig.2). The axial positions along the Oz axis are occupied by two DMF molecules bonded to the metal through their carbonyl oxygen atoms O [10].

Piroxicam adopts the N,O-coordination mode. Although an ambivalent liganting behaviour cannot be excluded, it should be noted that the observed N,O-chelation could be a reflection of the preference of transition - metal ions to form intramolecular mixedligand complexes by binding to ligands with heteroaromatic N residues and O donors [11].

Formation of the uncharged Cu-piroxicam species is of particular interest, since it has been shown that such neutral Cu-drug complexes are essential for effective distribution of the pharmacoactive agents and maintaining the copper balance in blood plasma [12].

4. Conclusion. The IR spectra of the antiinflammatory drugs and theirs Cu(II) complexes allowed us to establish two types of vibrations involved in complexation: i) vibrations whose frequencies are modified by participating at complexation and ii) new stretching vibrations such as ν_{Cu-O} and other combination bands.

The asymmetric and symmetric stretching vibrations of the COO- group appear in the 1550÷1760 cm^{-1} region. After complexation it was observed an appreciable shift in frequency, in agreement with the contribution to the coordination.

The values of the shifts for the COO^- group in metal complexes are: 130 cm^{-1} for Cu-aspirinate, 110 cm^{-1} for Cu-indomethacin and 140 cm^{-1} for Cu-ibuprofen.

Some vibrations such as the asymmetric and symmetric vibrations of the CH_3 and CH_2 groups, do not change the frequencies values after Cu(II) complexation. The bands assigned to these vibrations appear in the 2800÷3000 cm^{-1} region.

In the case of Cu(II)-indomrthacin compound appear two dimeric forms due to the different types of coordinations. This hypothesis is also supported by EPR measurements.

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STUDIA UNIV. BABEŞ-BOLYAI, PHYSICA, XXXVII, 2, 1992

CALCULATION ON ULTRASONIC DATA OF THE INCOMPRESSIBLE VOLUME AND OF THE FREE VOLUME IN BINARY LIQUID SYSTEMS

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ABSTRACT. - The calculation relationship of incompressible volume and free volume, corresponding to the elementary cell, resulted according to some models affected by approximations such as the acceptance of molecular arrangement in a cubic close packed quasicrystalline structure respectively of the free volume spherical form. These relationships have been verified on binary liquid systems: benzene-carbon tetrachloride, benzene-ethilene dichloride, acetone-chloroform and acetone-carbon sulphide as well as on the corresponding pure components at various temperatures. For this purpose we used our own experimental data concerning ultrasonic velocity, density, coefficient of thermal expansion as well as those of the adiabatic coefficient extracted from the table of constants.

1. Introduction. The molecular configuration structures of the liquids are determined by the equilibrium of intermolecular interaction potentials. Consequently, interactions are reflected by some physical factors which are correlated with the intermolecular free-length. In this context we can mention: refraction indices, density, ultrasonic velocity, compressibility and others.

Free volume, respectively excess value become criteria in interpreting intermolecular interactions in binary liquid mixtures.

Theoretical aspects. Formulated by Collins and Brandt, the state equation of free volume is given by:

$$P_i = \frac{RT}{V\left[1 - \left(\frac{V_0}{V}\right)\right]^{1/3}} \qquad (1)$$

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where P_i is internal pressure, R - perfect gases constant, T - temperature, V - molar volume, V_0 - incomporessible part of the molar volume.

Expressing the internal pressure by:

$$P_i = \frac{\rho c^2 \alpha T}{\chi} \tag{2}$$

from relationship (1) it results that:

$$\left(\frac{V_0}{V}\right)^{1/3} = \left(\frac{v_0}{v}\right)^{1/3} = 1 - \frac{R}{M}\frac{\chi}{\alpha c^2} \tag{3}$$

where M is molar mass, $\chi = \frac{C_P}{C_V}$, α - coefficient of thermal expansion, c - ultrasound velocity, v and v_0 represent the cell volume corresponding to a molecule, respectively its incompressible part.

The elementary cell free volume is expressed by:

$$v_f = k(l - d)^3 \tag{4}$$

where k is a form factor, l - distance between the centers of two molecules and d - the molecular diameter.

Relationship (4) by substitution $\frac{d}{l} = \left(\frac{v_0}{v}\right)^{1/3}$ and $\frac{l^3}{v} = f$

$$v_f = k\,f v\left[1 - \left(\frac{v_0}{v}\right)^{1/3}\right]^3 \tag{5}$$

When the arrangement is in a cubic close packed quasilattice system it results the relationship $f = \sqrt{2}$ and in case of a spherical form of the free volume where the radius is l-d, from relationship: (4) it results that k = $4\pi/3$ and consequently:

$$v_f = \frac{4\sqrt{2}\,\pi}{3} v\left[1 - \left(\frac{v_0}{v}\right)^{1/3}\right]^3 \tag{6}$$

3. Experimental. The calculations were extended to some binary liquid systems, including their respective components, thus, the incompressible volume as well as the free volume were determined in: benzene-carbon tetrachloride, benzene-dichloride ethilene, acetone-chloroform and acetone-carbon-sulphide at various concentrations and temperatures.

The thermal expansion coefficient, density and ultrasonic velocity within the mixtures obtained were measured by the method of optical diffraction in an ultrasonic system of 4 MHz.

In order to calculate the

$$\chi = 1 + \frac{M\alpha^2 c^2 T}{C_p}$$

was used, the values for C_p being extracted from the table of constants.

4. Results. Data obtained are shown in table I.

Table I.

Conc	T (K)	$P_i \cdot 10^{-5}$ (N/m^2)	$V \cdot 10^{-3}$ ($m^3/kmol$)	v_0 (A^3)	v_f (A^3)
χ_{CCl_4}			Benzene - carbon tetrachloride		
1	2	3	4	5	6
0	293	3748	88,90	117,6	0,340
	303	3657	89,97	117,69	0,396
	313	3567	91,06	117,74	0,477
	323	3476	92,27	117,91	0,530
	333	3393	93,44	118,00	0,609
	343	3304	94,72	118,13	0,702

1	2	3	4	5	6
0,2	293	3728	90,39	119,88	0,334
	303	3629	91,53	120,01	0,391
	313	3535	92,69	120,12	0,455
	323	3433	93,89	120,14	0,532
	333	3333	95,12	120,11	0,622
	343	3211	96,39	119,80	0,640
0,4	293	3649	92,13	122,21	0,340
	303	3665	93,10	122,04	0,399
	313	3469	94,33	122,21	0,465
	323	3373	95,51	122,19	0,542
	333	3269	96,85	122,27	0,635
	343	3157	98,16	122,06	0,749
0,6	293	3561	93,26	123,26	0,361
	303	3472	94,43	123,41	0,420
	313	3386	95,63	123,55	0,487
	323	3296	96,86	123,62	0,565
	333	3195	98,18	123,61	0,661
	343	3094	99,54	123,53	0,744
0,8	293	3492	94,89	125,35	0,369
	303	3396	96,08	125,41	0,433
	313	3315	97,29	125,56	0,501
	323	3219	98,55	125,55	0,586
	333	3121	99,88	125,52	0,625
	343	3021	101,23	125,37	0,803
1,0	293	3506	96,56	128,20	0,353
	303	3356	97,78	127,81	0,434
	313	3263	99,09	127,97	0,506
	323	3162	100,30	127,77	0,597
	333	3071	101,57	127,66	0,696
	343	2973	102,95	127,53	0,816
$\chi_{C_2H_4Cl_2}$		Benzene - dichloride ethilene			
0	293	3748	88,90	117,60	0,340
	303	3658	89,97	117,69	0,396
	313	3567	91,06	117,71	0,477
	323	3476	92,27	117,91	0,530
	333	3393	93,44	118,00	0,609
	343	3304	94,72	118,13	0,702

1	2	3	4	5	6
0,2	293	3804	87,24	115,29	0,338
	303	3721	88,27	115,41	0,396
	313	3642	89,36	115,60	0,448
	323	3538	90,49	115,57	0,524
	333	3443	91,59	115,49	0,607
	343	3344	92,85	115,52	0,705
0,4	293	3865	85,39	112,69	0,336
	303	3785	86,41	112,86	0,387
	313	3695	87,44	112,90	0,448
	323	3610	88,53	113,02	0,515
	333	3507	89,63	112,90	0,600
	343	3388	90,78	112,62	0,709
0,6	293	3971	83,46	110,26	0,323
	303	3878	84,46	110,35	0,358
	313	3778	85,46	110,32	0,438
	323	3705	86,50	110,50	0,499
	333	3597	87,65	110,51	0,582
	343	3499	88,52	110,05	0,677
0,8	293	4074	81,33	107,44	0,317
	303	4011	82,26	107,67	0,359
	313	3921	83,24	107,67	0,413
	323	3828	84,27	107,85	0,477
	333	3727	85,30	107,81	0,552
	343	3613	86,44	107,73	0,646
1,0	293	4237	79,01	104,63	0,298
	303	4179	79,93	104,94	0,336
	313	4089	80,86	105,03	0,386
	323	3997	81,85	105,15	0,444
	333	3898	82,86	105,19	0,502
	343	3802	83,88	105,90	0,574
χ_{CHCl_3}		Acetone - chloroform			
0	293	3413	73,31	89,56	0,663
	303	3304	74,38	88,31	0,865
	313	3211	75,49	89,19	0,915
	323	3099	76,61	88,76	1,086
0,2	293	3434	74,84	92,21	0,625
	303	3358	75,97	92,38	0,717
	313	3274	77,10	92,41	0,827
	323	3169	78,28	92,21	0,973

1	2	3	4	5	6
0,4	293	3424	77,69	95,12	0,600
	303	3342	77,75	95,11	0,694
	313	3259	78,84	95,07	0,802
	323	3176	79,93	94,93	0,928
0,6	293	3465	78,16	97,85	0,557
	303	3409	79,21	98,08	0,629
	313	3331	80,24	98,02	0,725
	323	3247	81,39	98,03	0,837
0,8	293	3600	79,48	101,09	0,480
	303	3515	80,55	101,18	0,556
	313	3420	81,58	101,02	0,648
	323	3328	82,70	100,96	0,752
1,0	293	3656	80,47	103,14	0,447
	303	3586	81,50	103,30	0,511
	313	3501	82,60	103,40	0,589
	323	3425	83,71	103,52	0,674
χ_{CS_2}		Acetone - carbon - sulphide			
0	293	3413	73,31	89,56	0,663
	303	3304	74,38	88,31	0,855
	313	3211	75,49	89,19	0,915
0,2	293	3380	71,44	86,26	0,718
	303	3279	72,41	85,91	0,847
	313	3194	73,51	85,84	0,980
0,4	293	3468	69,16	83,31	0,710
	303	3330	70,09	82,65	0,864
	313	3237	71,01	82,25	1,011
0,6	293	3527	66,78	79,94	0,724
	303	3410	67,67	79,47	0,863
	313	3287	68,44	78,62	1,037

1	2	3	4	5	6
0,8	293	3655	63,43	75,51	0,721
	303	3578	64,20	75,26	0,830
	313	3442	65,00	74,51	1,003
1,0	293	3821	60,29	71,62	0,698
	303	3749	61,00	71,40	0,798
	313	3665	61,77	71,13	0,919

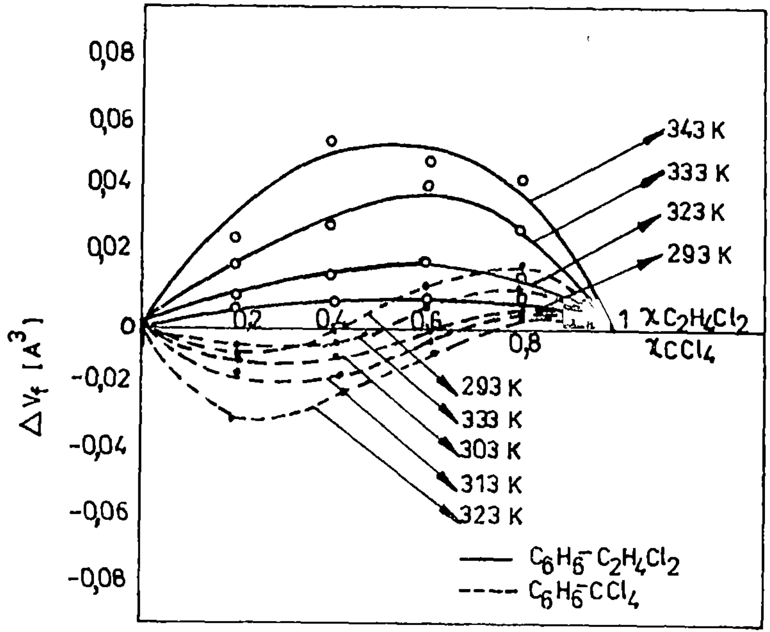

Figure 1

Free volume variation with the concentration at a constant temperature is marked by the posibility of some interactions occuring between the systems components; in′ order to put them into evidence excess values have been calculated from:

$$\nu_f - \nu_f(sist.) - [\nu_f(1) \cdot \chi_1 + \nu_f(2) \cdot \chi_2]$$

and the results are shown in fig. 1 and 2.

5. Discusions. The reasoning which led to the calculation of incompressible volume and of the free volume corresponding to the elementary cell is based on models affected by several

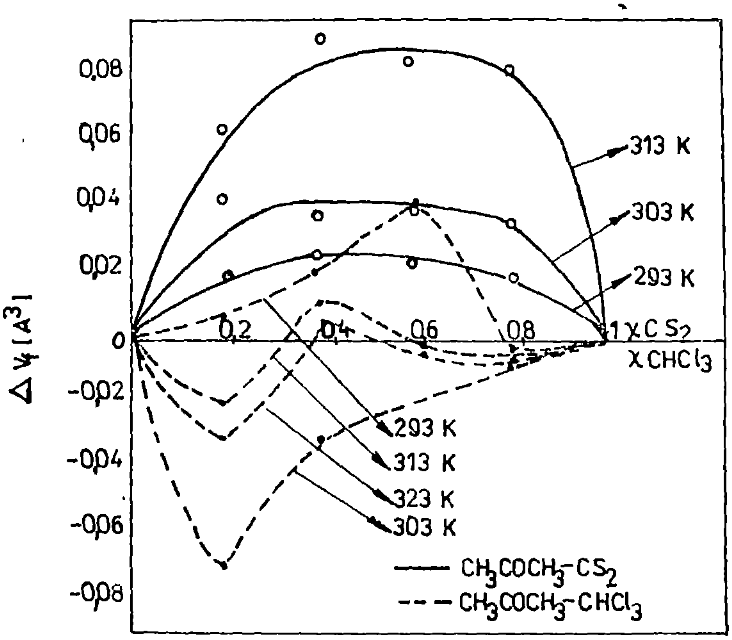

Figure 2

approximations such as: acceptance of molecule arrangement in a cubic close-packed quasi-crystalline structure respectivelly of the free volume spherical form. The results influenced by there approximations range within the limits corresponding to the magnitude orden, offering a geometrical reprezentation of molecular structures dependent on the intermolecular interaction potentials.

The independent temperature of incompressible volume as well as the increasing free volume according to the temperature, have to be mentioned.

Free volume variation, in close connection with concentration reflects the cooperative effects of intermolecular interactions as a consequence of interactions occuring between the system components emphasized by representing the additivity deviation.

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ESTIMATE OF INTERNAL PRESSURE CORRECTIONS OF LIQUIDS BY MEANS OF ULTRASONIC PROPAGATION VELOCITY

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ABSTRACT. - The correlation of various formulas of the internal pressure through their common parameter, the ultrasonic velocity, allowed the determination of correction factors regarding the rigorous expression of internal pressure in liquids. The relationships presented in this paper have been verified on the following organic liquids: benzene, carbon tetrachloride, ethane dichloride at temperatures ranging from 20°C to 70°C as well as on acetone, chlorophorme and carbon sulphide at temperatures from 20°C to 50°C. For this purpose we used our own experimental data for the ultrasonic velocity, density and coefficient of thermal expansion and those of the adiabatic coefficient are calculated on values from the table of constants.

1. Introduction. The internal pressure is presented in various formulas due to the use of different models or to the introduction of approximate calculation which is seen in the corresponding values discrepancy.

The establishment of the correction coefficients concerning the rigorous expression of the internal pressure implies the correlation of various formulas through the mechanisms that accompany volume variations of the medium. The internal pressure is defined by the modification of the potential energy corresponding to these volume variations.

2. Theory. The internal pressure defined by:

$$P_i = \left(\frac{\partial U}{\partial V}\right)_T \qquad (1)$$

is expressed as a function of the state parameters by the relation:

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$$P_i = T\left(\frac{\partial P}{\partial T}\right)_V - P_e \tag{2}$$

where: P_e is the external pressure that may by neglected in the case of liquids, except those undergoing great pressures.

After some transformations we obtain the calculable formula:

$$P_i = \frac{1}{\chi}\,\alpha\, T \rho\, c_S^2 = \frac{1}{\chi\,\beta_S}\,\alpha\, T \tag{3}$$

where: α is the coefficient of thermal expansion, ρ is the density, $\chi = C_p/C_O$, c_v is the ultrasound propagation velocity, and β_S is the adiabatic compressibility.

The Van der Waals internal pressure derives from a reasoning characterized by some approximation on the basis of a molecular model. Thus, limiting the interactions to the attraction throungh dispersion forces we can calculate the potential energy corresponding to all the pairs in a N number of molecules:

$$E_p = -\frac{2}{3}\pi N^2 \frac{A}{r_o^3}\frac{1}{V} \tag{4}$$

where: $\frac{2}{3}\pi N^2 \frac{A}{r_o^3} = a$ being considered a constant value it results

$$E_p = -\frac{a}{V} \tag{5}$$

respectively, from relation (1):

$$P_{i(w)} = \frac{a}{V^2} \tag{6}$$

In order to correlate $P_{i(w)}$ with the ultrasound propagation velocity defined by: $c_S^2 = (\partial P/\partial\rho)_S$ we use:

$$c_S^2 = -\chi\frac{V^2}{M}\left(\frac{\partial P}{\partial V}\right)_T \tag{7}$$

where neglecting the external pressure we obtain:

$$\int_{V_1}^{V_2} \frac{M c_S^2}{\chi\, V^2}\, dV = \frac{a_1}{V_1^2} - \frac{a_2}{V_2^2} \tag{8}$$

and for a narrow temperature range:

$$P_{i(w)} = \frac{1}{2\chi}\,\rho\, c_S^2 = \frac{1}{2\,\chi\,\beta_S} \tag{9}$$

Thus, from (3) and (9) ,we obtain the following:

$$P_i = 2\alpha T P_{i(w)} \tag{10}$$

where $2\alpha T$ represents the correction coefficient.

The Van der Waals internal pressure can be improved by the following expression of the internal energy:

$$E_{p(a)} = -\frac{a}{V^n} \tag{11}$$

whence:

$$P_{i(n)} = \frac{an}{V^{n+1}} \tag{12}$$

n is a typical liquid constant depending on temperature.

From condition $P_{i(n)} = P_i^{\cdot}$ it results the relation between the two corrections:

$$\frac{n}{V^{n-1}} = 2\alpha T \tag{13}$$

3. Experimental. The above mentioned relations were tested with the following organic liquids: benzene, carbon tetrachloride, carbon sulphide, acetone, chloroform and dichlorethylene.

We measured at various temperatures the ultrasound propagation velocity, at 4 MHz frequency, using the optical diffraction method. We also determined the coefficient of thermal expansion and the density. The values of $\chi = C_p/C_V$ were obtained from the relation:

$$\chi = 1 + \frac{M\alpha^2 c_s^2 T}{C_p} \tag{14}$$

for C_p we used constant tables.

4. Results. The data we obtained are shown in table I. For

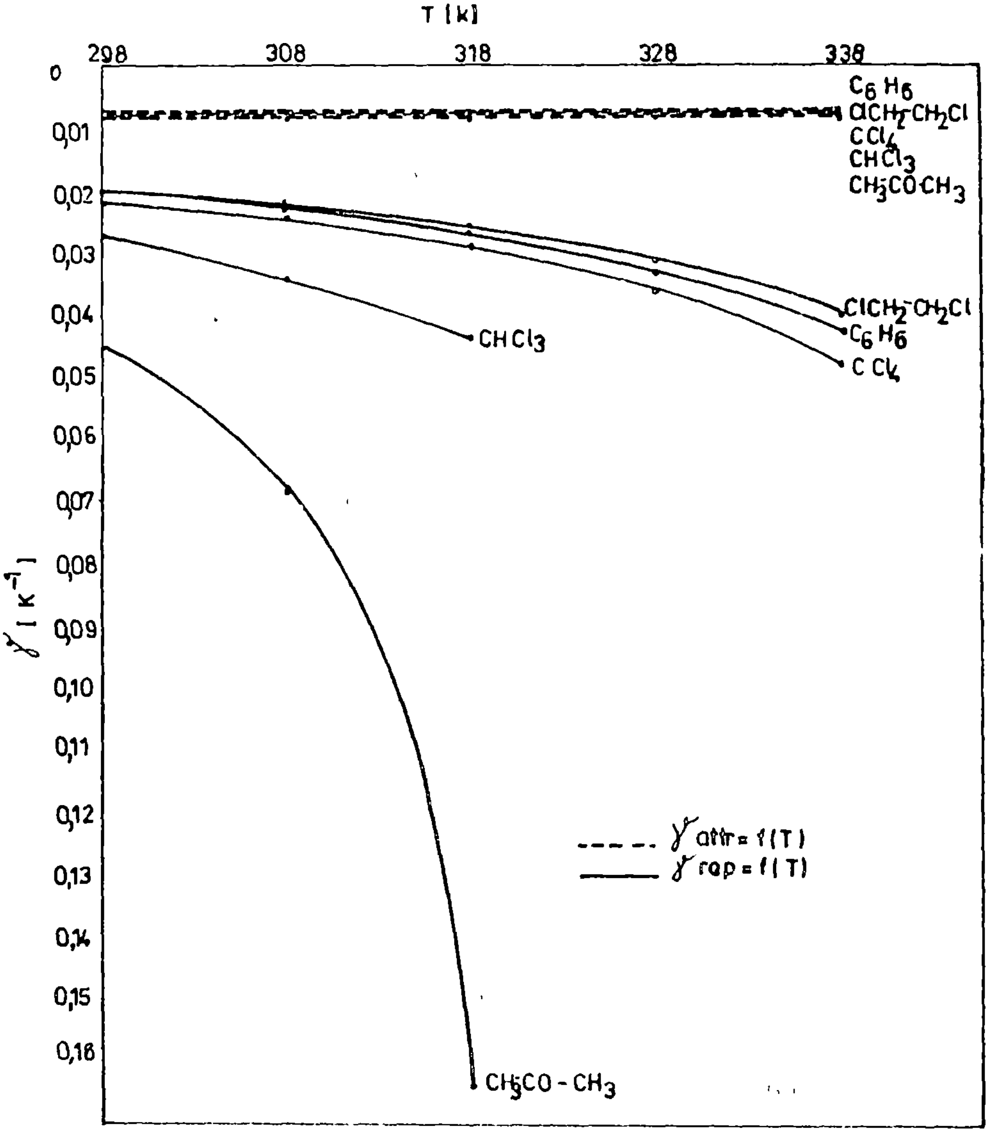

Figure 1

a comparison reason we presented in the last but one column the internal pressure values taken from the constant tables.

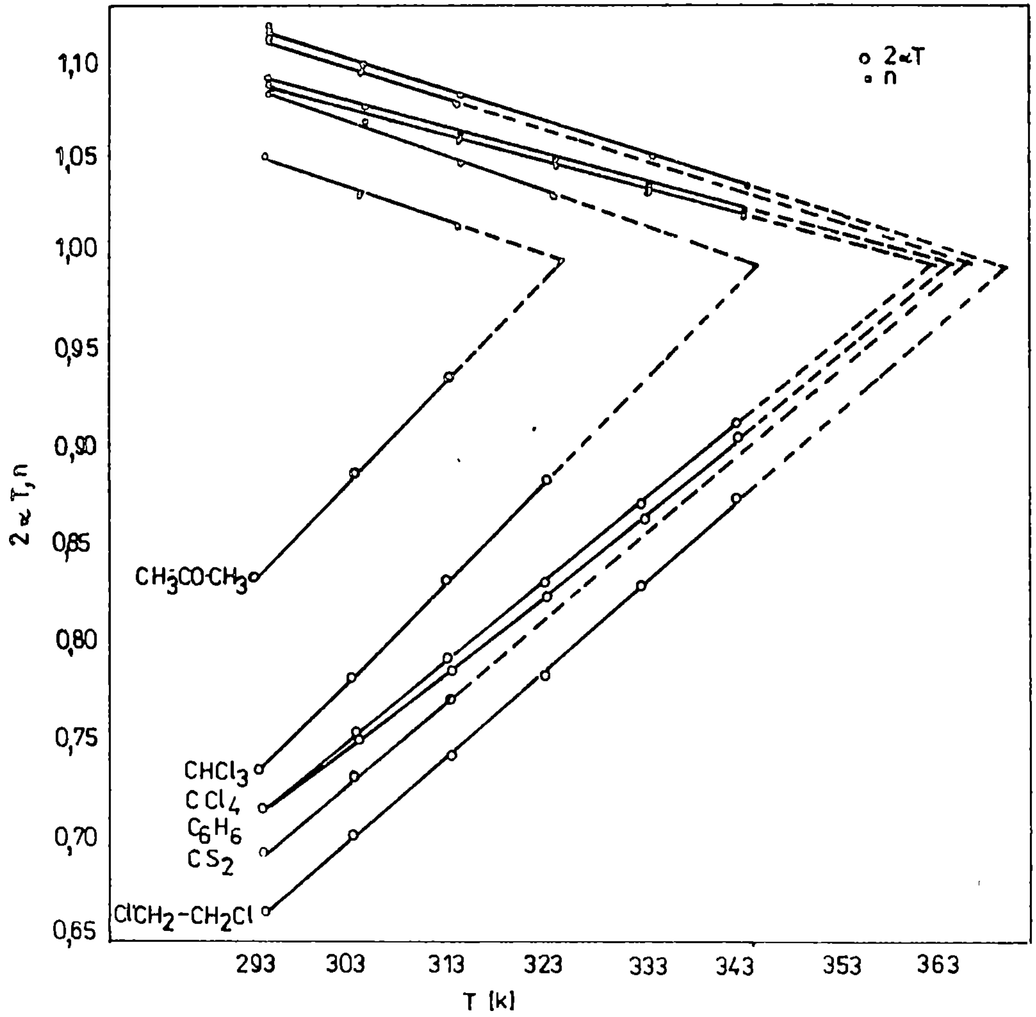

Figure 2

If we admit that the attraction intermolecular interactions in those liquids are exclusively caused by the dispersion forces, we have:

$$P_{i(att)} = P_{i(W)} \quad \text{then} \quad P_{i(rep)} = P_{i(W)} - P_i$$

The temperature dependence of these internal pressure components is shown in figure 1 by means of the coefficients:

$$\gamma_{(att)} = \frac{1}{P_{i(att)}} \frac{\partial P_{i(att)}}{\partial T}; \quad \gamma_{(rep)} = \frac{1}{P_{i(rep)}} \frac{\partial P_{i(rep)}}{\partial T}$$

at 1 atm. constant external pressure.

The variation as a function of temperature of the correction coefficients: $2\alpha T$ and n is shown in figure 2.

5. Discussion. The internal pressure values resulting from the calculation of the (12) relation are in agreement with the literature data, which confirms the validity of Van der Waals internal pressure correlation with the actual internal pressure through $2\alpha T$. The two correction coefficients are typical liquid values and depend on temperature.

From (10), (12), (13) relations, taking into consideration the absence of the rejecting component of the internal pressure from $P_{i(w)}$, we have: respectively $2\alpha T < 1$ and $n > 1$. The rise of $2\alpha T$, respectively the decrease of n as a function of temperature, according to the (13) relation, shows the interaction weakening when the intermolecular spaces grow, that of the rejecting one being more relevant; as a consequence, the α and $\frac{n}{V^{n-1}}$ values grow, because n decreases. The above mentioned remarks are valid for all kinds of intermolecular interactions, which is very important, especially in the liquid mixtures study.

The rise in temperature leads to a typical liquid value: $T_w = \frac{1}{2\alpha}$, in order to fulfil the limit condition: $2\alpha T = 1$, $n = 1$.

For this temperature, from:

$\frac{P_{i(rep)}}{P_{i(attr)}} = 1 - 2\alpha T_w = 1 - \frac{n}{V^{n-1}}$ it follows:

$P_{i(rep)} = 0$, respectively: $P_i = P_{i(w)}$.

Table 1

Liquid	T (K)	$2\alpha T$	$P_i(w)$ (atm) from (9)	P_i (atm) from (3)	P_i (atm) litera-ture	n from(13)
Benzene	293	0,71	5163	3700	3701	1,09
	303	0,75	4797	3611	3611	1,08
	313	0,79	4460	3521	3524	1,06
	323	0,83	4146	3431	3430	1,05
	333	0,87	3863	3350	3350	1,04
	343	0,91	3594	3262	3251	1,03
Carbon tetra-chloride	293	0,72	4743	3416	3416	1,09
	303	0,76	4373	3313	3313	1,07
	313	0,79	4049	3222	3221	1,06
	323	0,83	3739	3122	3121	1,05
	333	0,84	3462	3032	3032	1,04
	343	0,92	3198	2935	2936	1,02
Carbon sulphide	293	0,69	5404	3772	3772	1,11
	303	0,73	5031	3702	3700	1,09
	313	0,77	4672	3618	3618	1,08
Chloro-form	293	0,74	4865	3609	3608	1,08
	303	0,78	4493	3539	3539	1,07
	313	0,84	4133	3457	3458	1,05
	323	0,88	3812	3381	3380	1,03
Acetone	293	0,84	4016	3369	3265	1,05
	303	0,88	3671	3261	3148	1,03
	313	0,94	3372	3170	-	1,02
	323	0,99	3079	3059	-	1,00
Dichlor-ethylene	293	0,66	6305	4183	4182	1,12
	303	0,70	5864	4126	4124	1,10
	313	0,74	5419	4037	4039	1,08
	323	0,79	5006	3945	3944	1,07
	333	0,83	4619	3848	3850	1,05
	343	0,88	4264	3753	3758	1,04

In the case of the liquids with spherical symmetry moleculas and non-polar character, $P_{I(w)}$ and $P_{i(w)} - P_i$ represents the internal pressures corresponding to the cohesive forces, respectively the repulsive ones.

In order to describe their variation as a function of intermolecular spaces, we followed the temperature dependence of those coefficients: $\gamma_{(att)}$ and $\gamma_{(re\ )}$. It results that the temperature does not influence the $\gamma_{(att)}$ coefficient, which indicates, the linear decrease of the attraction internal pressure with temperature. The exponentially decrease of the absolute value of the $\gamma_{(rep)}$ coefficient corresponds to the range action of the repulsive force.

In the above reasoning the external pressure was considered constant, i.e.1atm.

The non-linearity of the variation in the intermolecular space as a function of temperature, issued from the rise in the coefficient of thermal expansion depending on temperature, is negligible comparately to the variation of the temperature coefficient of the internal pressure.

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philosophie (semestriellement)
sociologie-politologie (semestriellement)
psyhologie-pédagogie (semestriellement)
sciences, économiques (semestriellement)
sciences juridiques (semestriellement)
histoire (semestriellement)
philologie (triemestriellement)
théologie orthodoxe (semestriellement)

43 904

Lei 200