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THE ELECTRICAL BEHAVIOUR OF THE M_xHgI_4 INORGANIC COMBINATION AND SOME STRUCTURAL ALTERATIONS VERSUS THE PRESSURE

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ABSTRACT

In this paper the structural changes of the M_xHgI_4 - type combinations ($M = Ag^+, Cu^+, Tl^+, Pb^{2+}, Cd^{2+}$ and $x = 1,2$) which occur due to pressure (5 - 30 MPa) applied on the powder of these complexes are presented.

These alterations were confirmed by the X - ray diffraction spectra and by electrical conductibility measurements.

RESUMO

Este trabalho trata de mudanças estruturais que acontecem quando pó de complexos do tipo M_xHgI_4 onde ($M = Ag^+, Cu^+, Tl^+, Pb^{2+}, Cd^{2+}$ e $x = 1,2$) está sujeito a pressões de 5 a 30 MPa.

Estas alterações estruturais foram confirmadas por espectra de difração de raios-X e medidas de condutibilidade elétrica.

KEYWORDS : tetraiodomercurates, electrical conductibility, X-ray diffraction, structural alterations.

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INTRODUCTION

The structure of the α and β crystalline phases of the Ag_2HgI_4 and Cu_2HgI_4 compounds has been known from the papers initiated by Ketelaar in 1931 - 1938[1-5] and studies continued in the fifties and sixties by Frevel[6], Suchov[7], Hahn[8], Otsuba et al.[9]

Some relationships between the structure and the electrical conductibility, versus either the temperature or the pressure or both of them simultaneously, within the inorganic M_xHgI_4 (where $M = Ag^+, Cu^+$)[10,11] combinations class were established in the period of 1964 - 1974.

Between 1974 and 1975, Kasper and Browall[12,13] determined the structure of the Ag_2HgI_4 monocrystals both for the low temperature crystalline phase - β (ordered) and for the high temperature crystalline phase - α(disordered).

Olson and Harris[14] also performed these determinations on polycrystalline species. In 1982, the relationship structure - electrical conductibility versus the temperature and pressure for the inorganic Tl_2ZnI_4 combination was studied using Raman Spectra, by McOmber - et al[15].

Another paper, elaborated by Brightwell and Buckley in 1984[16], presents the equilibrium phase diagram for the AgI-CdI_2 system compared to the Ag_2HgI_4 and Ag_2ZnI_4 compounds.

In this paper the structural modifications of the M_xHgI_4 inorganic combinations versus the nature of the metallic M^{n+} ion, were studied using the X - ray diffraction and electrical conductibility measurements. The paper also established the structural lattice changes of the respective compounds and the effects on the electrical conductibility, when the microcrystalline powders are exposed to some certain pressure (5-30 MPa) for definite periods.

EXPERIMENTAL PART

An X-ray diffraction type TUR-M-62 apparatus equipped with a HZG-3 diffractometer operating with CuK_α radiation was used. The X-ray excitation was performed at 30 kV and 30 mA. The moving rate of the counter arm of the diffractometer was 0.5° Bragg/min; range was 1.5-25° Bragg. The intensity scale expressed in qpm (quants/min) was selected so that the most intense diffraction line was totally included into the diffractogramme. The measuring of the diffraction lines precision was ±0.005° Bragg.

The electrical conductibility measurements were performed through the "four wells" method[17] using a "Coucusai" French type apparatus. The wells used in performing the determination are made of wolfram and they are fixed using some sapphire bearings. The bearings are positioned collinearly, the distance between them being 1mm.

After being obtained through wet synthesis, the M_xHgI_4 compound were filtered, washed with alcohol and then dried with P_2O_5. The microcrystalline powders were used for further determinations, as follows:

- in order to perform the diffractometric study, microcrystalline powders samples and pellets (cylindrical samples), were obtained from the powder, using a DP-36 (D.R.G.) press. at the following values: 1; 5; 10; 15; 20 and 30 MPa;
- in order to study the electrical conductibility, σ , pellets obtained at the above partial pressures were used for all the five M_xHgI_4 compounds studied. X-ray diffraction data and electrical conductibilities were obtained at room temperature.

RESULTS AND DISCUSSION

The results obtained through the determination of the electrical conductibility, σ, for all the M_xHgI_4 compounds studied.

The Figures 1a - 2a present the electrical conductibility, σ, versus the pressure, P. It can be observed that the electrical conductibility for the Ag_2HgI_4, Cu_2HgI_4 compounds exhibits maxima at a 15 MPa and 20 MPa, respectively. These maxima are in accordance with the determinations performed by R. Well and coworkers[10] for Ag_2HgI_4, by S. Shibata et al.[11] for Cu_2HgI_4 and by McOmber et al.[15] for both of these compounds. Moreover, a second maximum of the electrical conductibility was found for the Ag_2HgI_4 compound, at 25 MPa. The Tl_2HgI_4 and $PbHgI_4$ compounds exhibit a decrease of electrical conductibility with increasing pressure (Fig. 3a and 4a), and the Cu_2HgI_4 compound exhibits maximum values of the electrical conductibility at 30 MPa (Fig. 5a).

The diffraction spectra performed on the M_xHgI_4 compounds do not confirm this supposition. Thus, the diffractogrammes obtained on the respective samples (Tables 1-5), at different pressure, did not lead to the conclusion of a phase transformations, with a change of the diffraction spectrum.

Tables 1-5

All these determinations are in accordance with the observations made by the Omber and coworkers[15] and Greig and collaborators[19]. They didn't observe any changes in the Raman spectra of the Ag_2HgI_4 , Cu_2HgI_4 compounds as a function of pressure in the range of the pressure values mentioned above. This confirmed that a new crystalline phase didn't appear. $d_o$hkl values sets resulted from the diffractogrammes obtained on the powders and $d_p$hkl values sets were obtained from the diffractogrammes on the same compounds pressed under different pressures. The experimental values |Adhkl| = $d_p$hkl - $d_o$hkl (axial parameter referring to the distance between two atomic planes) were calculated using these values sets and graphic represented versus the pressing pressure (Fig. 1b-5b).

Figures 1a,b-5a,b.

These Figures are different for different compounds, but are similar for the same compounds and can be compared to the 1a-5a Figures. Therefore, it can be assumed that the electrical conductibility alteration is determined by some order - disorder phenomena, in relation with the reticulate crystalline planes. (i.e. the number of atoms and holes, within the respective planes, without an alteration of the respective cell unit)

The diffraction spectra of the samples at different pressure are presented in Tables 1-5. It can be appreciated that some alterations of the crystalline lattice appear with the increasing pressure, meaning the appearance or the disappeareance of same spaces, towards which the metallic ions can move or not, determining an increase or a decrease of the total conductibility. The qualitative assumptions regarding to the

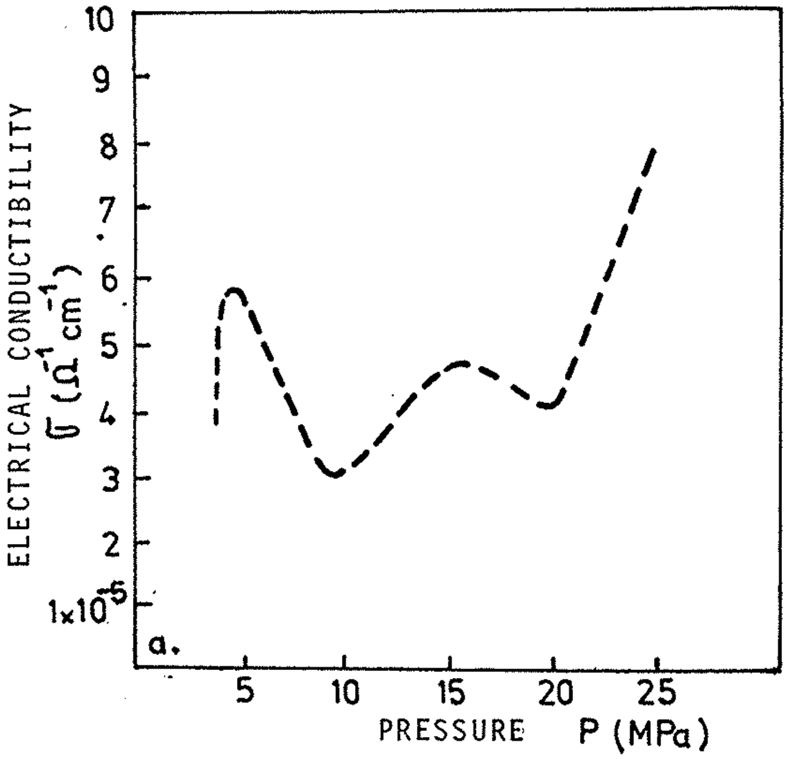

Fig. 1a-The electrical conductibility versus pressure for the Ag_2HgI_4 compound.

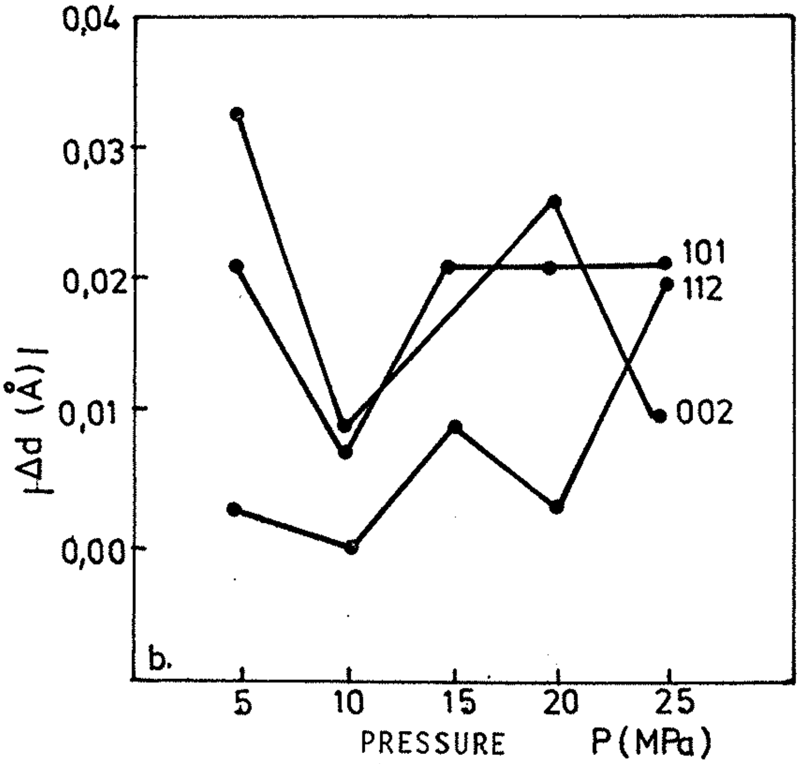

Fig. 1b-The |Δd(A)| parameter versus pressure for the Ag_2HgI_4 compound.

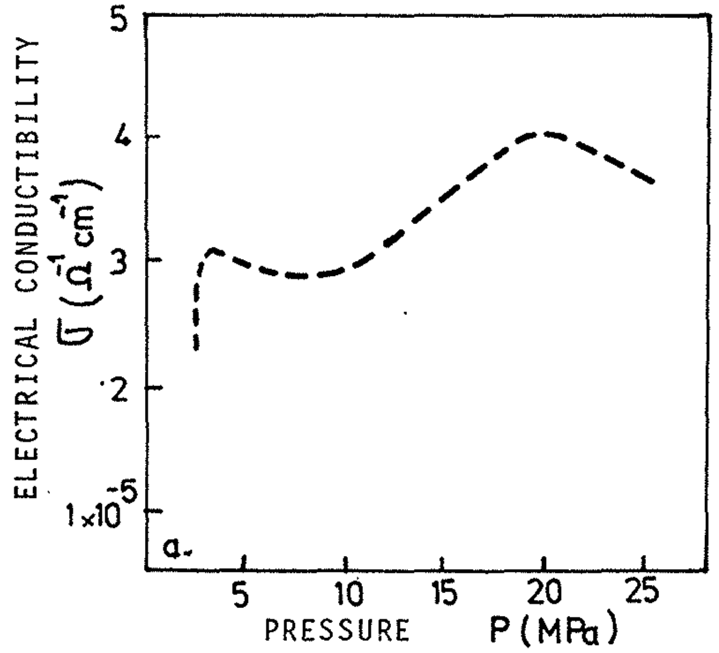

Fig.2a-The electrical conductibility versus pressure for the Cu_2HgI_4 compound.

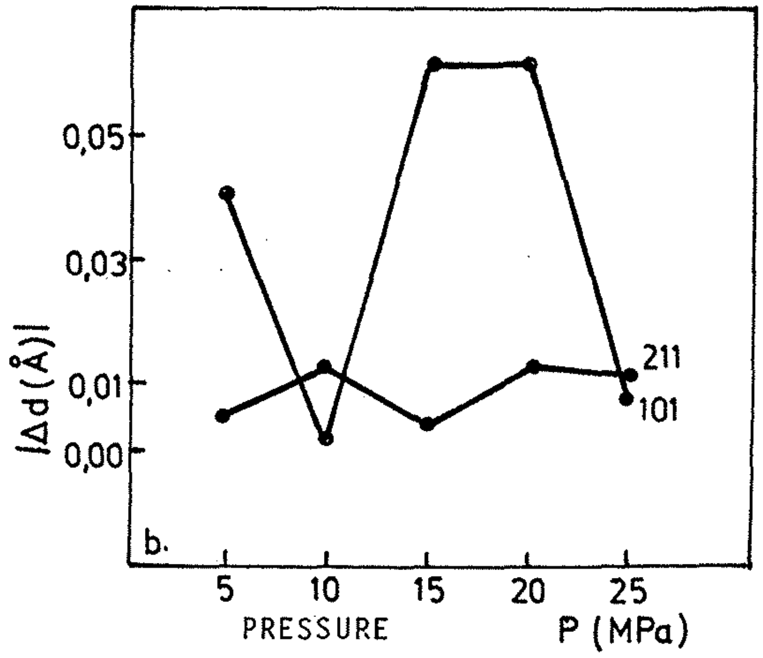

Fig.2b-The |Δd(A)| parameter versus pressure for the Cu_2HgI_4 compound.

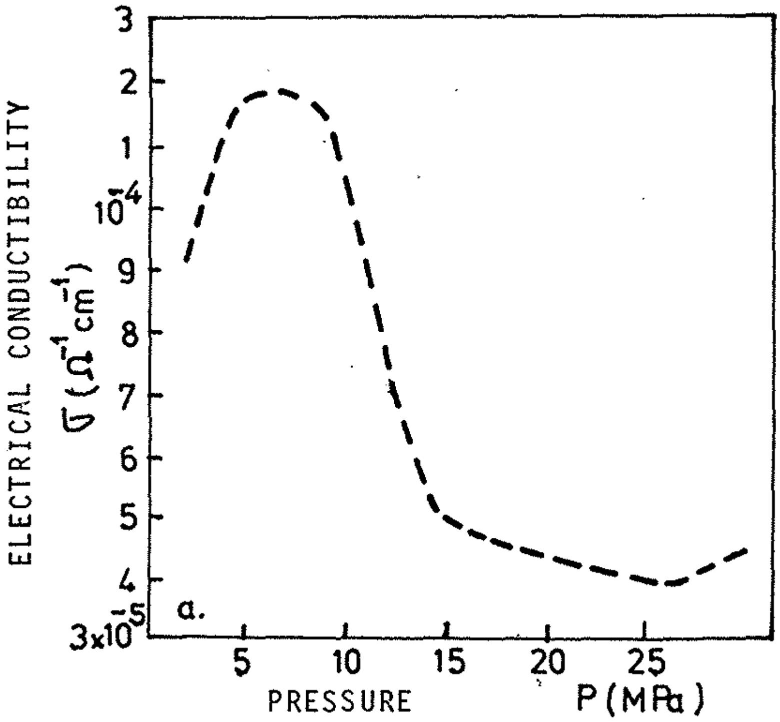

Fig.3a-The electrical conductibility versus pressure for the Tl_2HgI_4 compound.

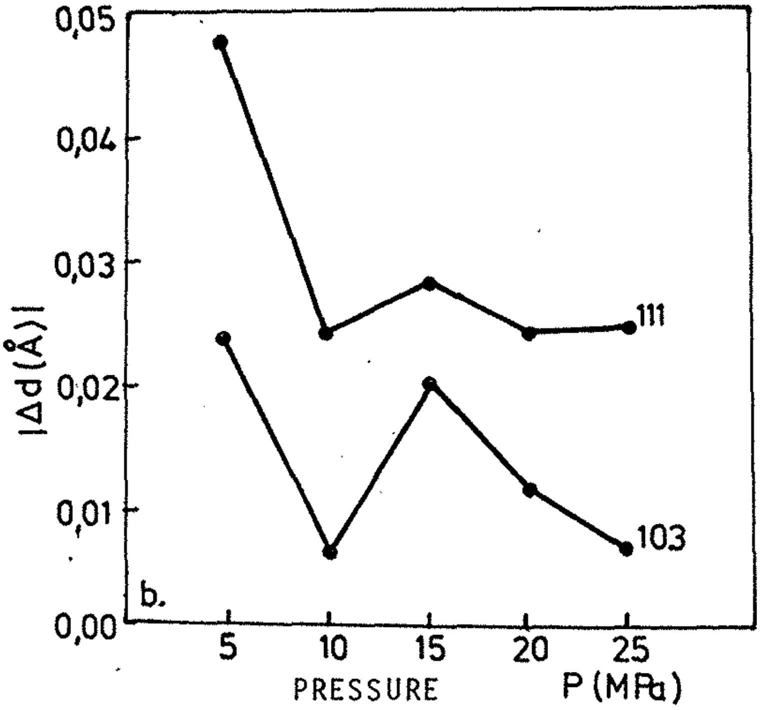

Fig.3b-The |Δd(A)| parameter versus pressure for the Tl_2HgI_4 compound.

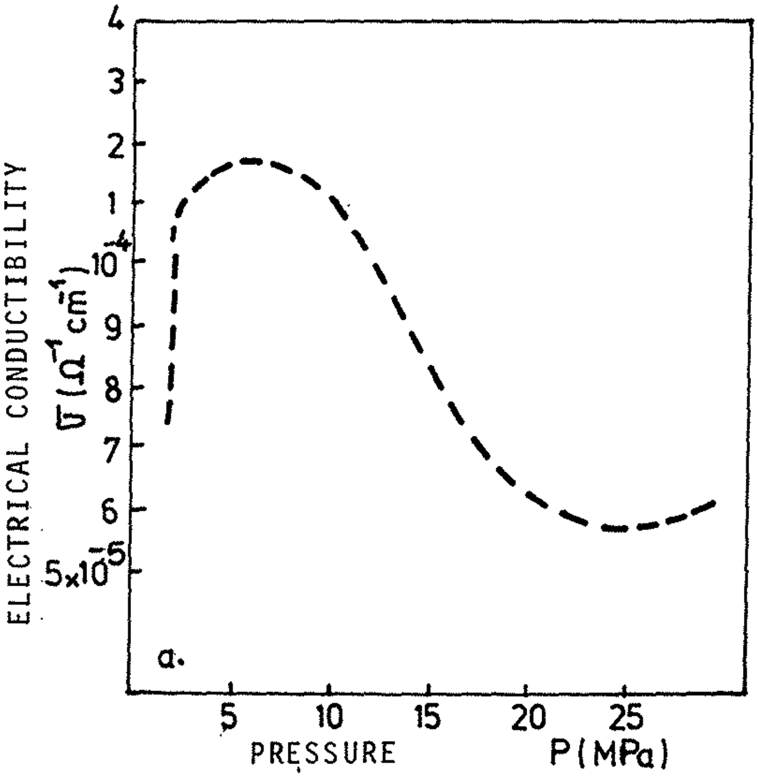

Fig.4a-The electrical conductibility versus pressure for the $PbHgI_4$ compound.

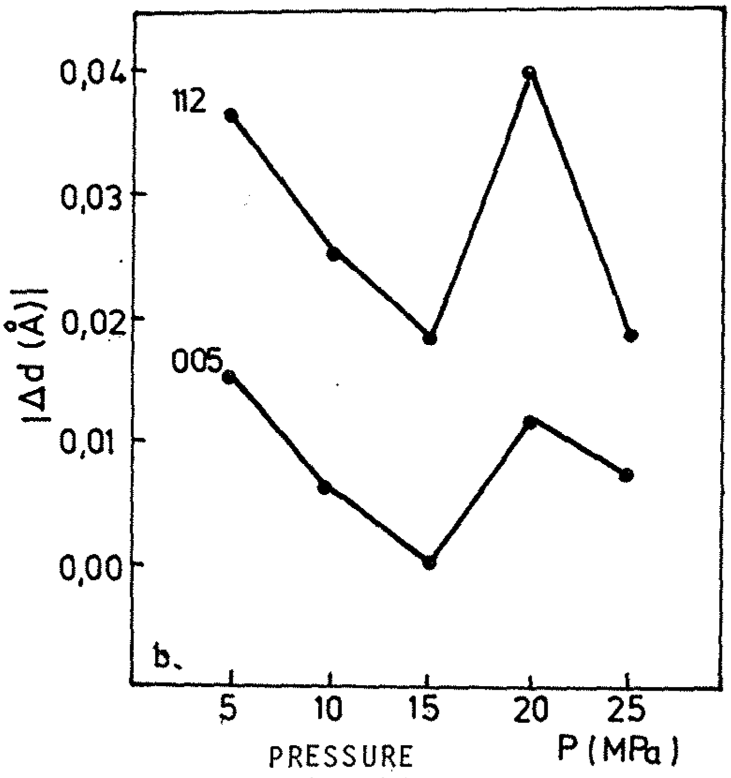

Fig.4b-The $|\Delta d(A)|$ parameter versus pressure for the $PbHgI_4$ compound.

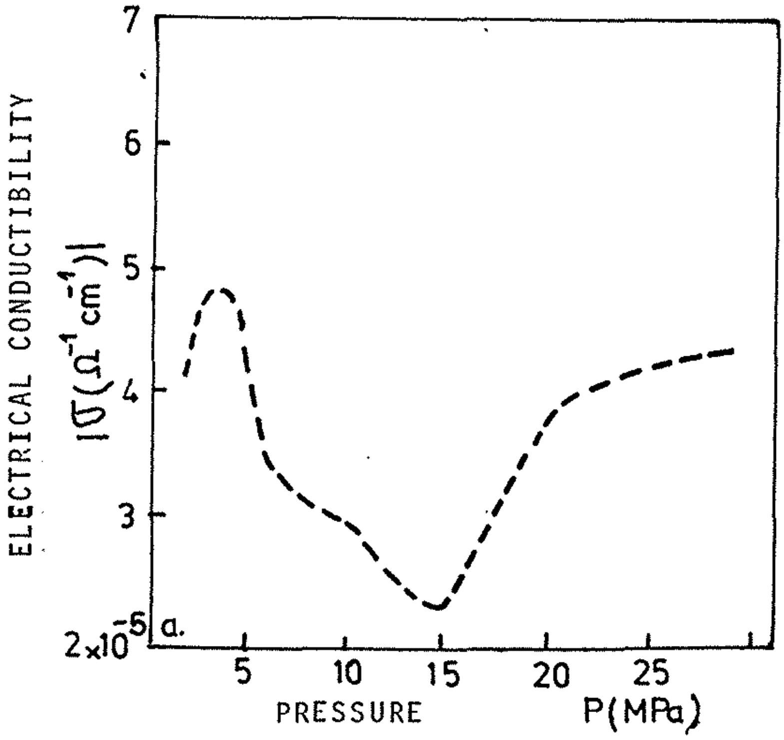

Fig.5a-The electrical conductibility versus pressure for the $CdHgI_4$ compound.

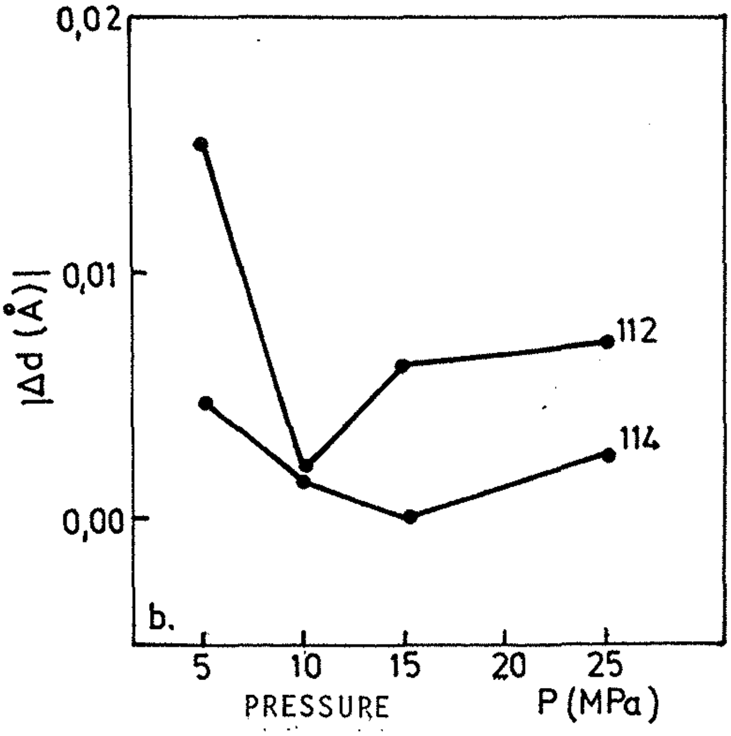

Fig.5b-The |Δd(A)| parameter versus pressure for the $CdHgI_4$ compound.

TABLE 1 - X-Ray diffraction data for powder - Ag_2HgI_4 compound and powder under pressure effect

P, MPa												
0			5		10		15		20		25	
d_0, Å	I/I_1	hkl	d_p, Å	I/I_1	d_p, Å	I/I_1	d_p, Å	I/I_1	d_p, Å	I/I_1	d_p, Å	I/I_1
6,2668	14	002	6,3000	12	6,2757	14	6,2492	14	6,2405	16	6,2580	13
									5.9644	14		
5.6253	19	101	5,6467	13	5,6182	25	5,6041	19	5,6467	22	5,6041	16
									4.5253	16		
4,4622	16	110	4,4711	15	4,4533	19	4,4533	19	4,4622	16	4,4313	15
3,6390	100	112	3,6419	100	3,6390	100	3,6302	100	3,6419	100	3,6186	100
3,4981	16	103	3,4954	12	3,4954	17	3,4847	18	3,5036	19	3,4740	14
2,8184	16	202	2,8236	13	2,8219	19	2,8167	24	2,8289	19	2,8115	14
2,7525	15	211	2,7542	13	2,7608	19	2,7378	24	2,7592	18	2,7460	14
2,5728	14	212	2,5771	11	2,5743	17	2,5671	19	2,5786	16	2,5671	13
2,3433	14	213	2,3480	11	2,3374	17	2,3386	19	2,3456	15	2,3386	14
2,2317	49	220	2,2328	38	2,2338	54	2,2275	73	2,2349	50	2,2222	48
2,1040	16	222, 300	2,1007	11	2,1010	16	2,1000	17	2,1100	15	2,1000	14
1,9239	28	312	1,9079	16	1,9087	29	1,9004	38	1,9095	30	1,9012	34
1,9034	28	116	1,9004	16	1,9034	31	1,8952	38	1,9034	29	1,8959	34

TABLE 2 - X-Ray diffraction data for the powder - Cu_2HgI_4 compound and powder under pressure effect

P, MPa												
0			5		10		15		20		25	
d_0, Å	I/I_1	hkl	d_p, Å	I/I_1	d_p, Å	I/I_1	d_p, Å	I/I_1	d_p, Å	I/I_1	d_p, Å	I/I_1
5,4399	14	101	5,4800	5	5,4399	22	5,5003	25	5,5003	24	5,4433	34
3,5172	100	112	3,5282	100	3,5036	100	3,5227	100	3,5309	100	3,4700	100
3,3857	14	103	3,4035	6	—	—	3,3907	28	3,3984	24	3,3756	31
—	—	—	3,2452	7	—	—	—	—	—	—	—	—
—	—	—	3,1728	8	—	—	—	—	—	—	—	—
—	—	—	3,1099	7	—	—	—	—	—	—	—	—
—	—	—	3,0659	7	—	—	—	—	—	—	—	—
3,0500	16	200, 004	3,0475	6	—	—	—	—	—	—	—	—
2,7592	10	104, 202	2,8030	5	—	—	2,7708	25	—	—	—	—
2,6542	12	211	2,6588	5	2,6420	28	2,6526	25	2,6649	24	2,6450	30
2,2618	10	105, 213	—	—	—	—	—	—	—	—	2,2275	30
2,1562	24	220, 204	2,1581	10	2,1532	40	2,1552	45	2,1611	39	2,1522	47
2,1454	20	115, 221	—	—	2,1493	35	2,1445	40	2,1450	35	2,1480	47
2,0651	8	224, 006	2,0777	8	2,0696	25	2,0768	25	2,0777	21	—	—

TABLE 3 - X-Ray diffraction data for the powder - Tl_2HgI_4 compound and powder under pressure effect

P, MPa														
0			5		10		15		20		25			
d_e, Å	I/I_1	hkl	d_p, Å	I/I_1	d_p, Å	I/I_1	d_p, Å	I/I_1	d_p, Å	I/I_1	d_p, Å	I/I_1		
6,5823	19	002	6.6810	18	6.5726	18	6,6019	22	6,6019	20	6,6019	20		
4,6091	15	102	4,6571	12	4.6187	18	4,6474	24	6,6474	18	4,6474	15		
4,1990	15	111	4,2466	20	4,2227	18	4,2267	24	4,2227	22	4,2227	18		
3,5643	41	103	3,5785	12	3,5699	14	3,5841	38	3,5756	37	3,5699	33		
3,3309	20	004	3,3581	36	3.3334	26	3.3432	38	3,3309	35	3,3309	22		
3.1120	100	201	3.1356	100	3,1184	100	3,1227	100	3,1163	100	3,1163	100		
2,9838	61	104	2,9994	107	2,9818	79	2,9955	81	2.9818	90	2,9838.	69		
2,9227	15	202	2,9434	16	2.9302	16	2,9377	22	2,9321	18	2,9265	20		
2.7625	19	211	—	—	—	—	2,7661	24	2,7658	22	2,7625	20		
2,6110	13	203	2,6300	15	—	—	—	—	2,6121	14	—	—		
2,4870	13	105	2,4952	15	2,4806	12	—	—	—	—	—	—		
2.3563	19	213	2,3659	18	2,3539	16	2.3622	22	2,3587	17	2.3575	18		
2,3120	22	204	2,3200	18	2,3109	19	2.3212	22	2.3109	18	2.3120	22		
2,2727	17	115	2.2849	18	2,2749	16	2,2838	19	2,2716	16	2.2750	18		
2,2222	17	221	2,2328	22	2,2201	21	2,2296	27	2,2212	20	2,2222	20		
2,1920	24	006	—	—	2,1902	19	2,1943	30	2,1902	41	2.1902	27		
2.1100	17	301	2.1176	25	2,1110	19	2,1157	24	2.1100	20	2.1100	22		
2,0650	32	302	2,0561	24	2,0482	19	2.0535	24	2,0499	22	2,0490	21		

TABLE 4 - X-Ray diffraction data for the powder - $PbHgI_4$ compound and powder under pressure effect

P, MPa													
0			5		10		15		20		25		
d_o, Å	I/I_1	hkl	d_p, Å	I/I_1	d_p, Å	I/I_1	d_p, Å	I/I_1	d_p, Å	I/I_1	d_p, Å	I/I_1
6,964*	100	—	7,0303*	100	7,0081*	100	6,9971*	100	7,0415*	100	7.0192*	100
6.553	10	002	6,6019	12	6,5824	18	6,6216	13	6.6414	14	6.6414	16
4,2913	10	003	4,3078	12	4,2910	20	4,2954	13	4.3161	16	4,3078	16
4.0220	8	112	4,0586	12	4,0476	20	4,0404	13	4.0623	14	4.0404	16
3,3330	15	201	3,3482	19	3,3482	29	3.3408	18	3,3556	23	3.3432	25
3,2804	13	044	3.2995	16	3,2971	25	3,3019	17	3,2971	20	3.2932	22
2,6992	10	203	2.7120	13	2,7104	20	2,6992	11	2.7071	14	2.7104	17
2,6345	8	005	2,6496	12	2,6405	20	2,6345	13	2.6465	16	2.6420	17
2,4012	7	221	2,5033	10	2,4979	16	—	—	—	—	—	—
2,1415	9	311	2,1490	12	2,1434	14	2,1466	11	2.1434	11	2.1450	16

* The most intense spectral line belongs to the PbI_2 compound (JCPDS 7-235) and not to $PbHgI_4$ compound

TABLE 5 - X-Ray diffraction data for the powder - $CdHgI_4$ compound and powder under pressure effect

P, MPa										
0			10		15		20		30	
d, Å	I/I_1	hkl	d_p, Å	I/I_1	d_p, Å	I/I_1	d_p, Å	I/I_1	d_p, Å	I/I_1
6,2317	83	002	6,2143	188	6,2317	118	6,2230	124	6,1712	90
4,1106	76	101	4,1257	54	4,1409	61	4,1219	64	4.1031	57
3,5756	100	102	3.5756	100	3,5756	100	3,5784	100	3.5587	100
3.1120	21	004	3,1120	11	3.1099	9	3.1099	11	3,0867	10
3,0014	48	103	3.0113	56	3.0073	46	3,0093	49	2.9955	47
		111								
2,7625	41	112	2,7741	17	2,7641	13	2,7675	19	2,7558	17
2,5265	24	104	2,5334	15	2,5320	9	2,5334	13	2,5224	13
2,1902	55	114	2,1953	33	2,1922	21	2.1902	36	2.1871	28
2,1871	29	200	2,1892	33	2.1861	25	2.1851	34	2.1780	30
2,1581	28	105	2,1601	25	2.1591	22	2,1611	17	2,1571	17
2,0695	31	202,	2,0741	35	2,0750	28	2,0741	29	2,0677	24
		006								
1.9285	28	211	1,9324	12	1.9324	9	1,9309	10	1.9247	12
		203								
1.8732	31	106	1,8717	12	1.8725	12	1.8753	14	1.8695	13
1,8609	31	212	1,8660	12	1,8645	9	1,8631	11	1.8568	15

explanation of the electrical conduction within the inorganic type M_xHgI_4 combinations consider the metallic ion mobility[18] and also the preferential tendency of increasing of the crystalline cell-unit reticulate parameters, both on "a" or "c" direction.

β-Ag_2HgI_4 and β- Cu_2HgI_4 phases are structurally identical in accordance with the literature data. A similarity between the shapes of the electrical conductibility versus pressure diagrams and the shapes of the $|\Delta d(hkl)|$ diagrams can be noticed. The diagrams in Figures 1a,b-5a,b show a correlation between the electrical conductibility and the $|\Delta d(hkl)|$ values, leading to the conclusions that the appearance or disappearance of some spaces within the crystalline lattice can contribute to the alteration of the electrical conductibility.

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