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PHASE TRANSITION IN MnF_2 *AT HIGH PRESSURE*

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An x-ray investigation of the effect of high pressure on the structure of MnF_2 is carried out up to 80 kbar. It is found that a reversible phase transition of the initial MnF_2 phase with a rutile-like structure occurs when $p > 20-30$ kbar. On the basis of the obtained data, it can be assumed that the high-pressure MnF_2 phase has a distorted structure of the CaF_2 type, which is close to the structure of the tetragonal ZrO_2 modification. It is shown that after removing the pressure a metastable phase with a structure of the α-PbO_2 type is formed from the phase which is stable at high pressure; the metastable phase is thus not the high-pressure phase as was previously assumed.

IT is well known that Azzaria and Dachille[1] observed a new MnF_2 modification isostructural with α-PbO_2; the new phase was obtained at a pressure of ~20 kbar and a temperature ~200 °C from the initial rutile-structure modification of MnF_2. Subsequently Kabalkina and Popova[2] showed that this phase (we shall refer to it as "α-PbO_2") is stable in a wide range of pressures and temperatures, up to 140 kbar and $t \approx 1700$ °C (the upper limit on the experimental conditions); under usual conditions the "α-PbO_2" phase is metastable.

The increased interest in MnF_2 is due to the fact that on the basis of the simplest crystal-chemistry considerations (the ratio of the ionic radii close to the upper limit of the stability of rutile) one might have assumed that at high pressures an MnF_2 phase should exist with coordination number 8 (a CaF_2 structure or a structure close to it). At first sight the results of the indicated papers exclude such a possibility; in the "α-PbO_2" phase, as in rutile, the coordination number is 6 and both structures differs only in the motif of positions of the cations.[3] It should, however, be noted that the method of investigation in papers [1,2] made it possible to determine the structure of the substance only after removal of the pressure and reduction of the temperature. Actually in both cases the investigation was carried out as follows: after the effect of the temperature and pressure on the MnF_2 with a rutile structure the substance was taken out from the high-temperature apparatus and was analyzed by means of x rays under normal conditions (atmospheric pressure and room temperature); an RKU-114 camera was used to obtain Debye-Scherrer powder patterns. As a result, it remained unclear whether the "α-PbO_2" phase is obtained at high pressures directly from the rutile modification and is retained at $p = 1$ bar in a metastable state, or whether it is formed after the removal of the pressure from the high-pressure stable phase; the latter would mean that a transition from rutile to an X phase transition occurs at high pressure, where X is a stable high-pressure phase different from "α-PbO_2."

The purpose of this paper was to attempt to determine the condition under which MnF_2 with an α-PbO_2 structure is formed.

The method used in the investigation allowed one to obtain x-ray patterns directly at high pressures up to 100 kbar in a special camera.[4,5] The main part of the camera is a pellet of amorphous boron with a channel for the sample, situated between two anvils of VK-6 hard alloy. Pressure calibration was carried out by determining the discontinuities of the electrical resistance of bismuth at the phase transitions at 25.4, 27, and 88 kbar.[6]

The investigation of the effect of high pressure on the MnF_2 (rutile) phase led to the following results:

1. At $p = 20-30$ kbar a phase transition was observed from the rutile structure to the X structure, the data for which are presented in Table I.
2. After removal of the pressure the "α-PbO_2" phase was always obtained with a small admixture of the rutile modification (the x-ray pattern is the same as in [1,2]).

It has thus been shown that the "α-PbO_2" phase is formed after the removal of the high

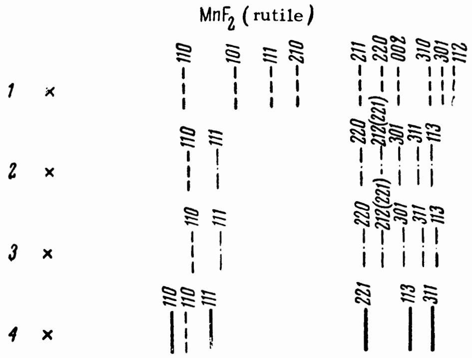

FIG. 1. Schematic diagram of the diffraction patterns of MnF_2 (the initial phase was rutile) at various pressures: 1 – p = 1 bar – rutile phase, 2 – p = 30 kbar – mixture of the rutile phase with phase X, 3 – p = 60 kbar – mixture of the X phase and rutile, 4 – p = 1 bar – mixture of the "α-PbO_2" phase with rutile. Notation: dashed lines belong to the rutile phase, continuous lines belong to the phase with the "α-PbO_2" structure, dash-dot lines belong to phase X. The cross denotes the position of the primary beam on the photographs.

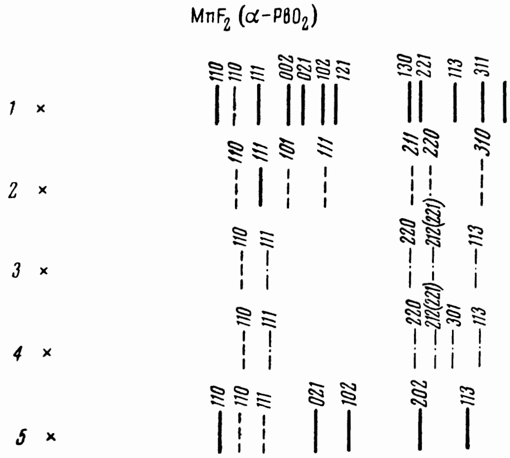

FIG. 2. Schematic diagram of the diffraction patterns of MnF_2 (the initial phase was "α-PbO_2") at various pressures: 1 – p = 1 bar – "α-PbO_2" phase with an admixture of rutile, 2 – p = 27 kbar – rutile with admixture of "α-PbO_2", 3 – p = 37 kbar – phase X with admixture of rutile, 4 – p = 47 kbar – phase X with admixture of rutile, 5 – p = 1 bar – "α-PbO_2" phase with admixture of rutile. Notation: dashed lines belong to MnF_2 with rutile structure, continuous lines belong to MnF_2 with "α-PbO_2" structure, and dash-dot lines belong to MnF_2 with X structure.

pressure ($p \geq 20$ kbar) at room temperature.

We also investigated the effect of high pressure on the MnF_2 phase isostructural with α-PbO_2. The starting material in this case was the product obtained in [2].[1] In all, 85 experiments were carried out in the range of pressures up to ~80 kbar.

The obtained data show that at low pressures, up to 30 kbar approximately, a phase transition is observed of the initial material with the α-PbO_2 structure into a phase isostructural with rutile (the "α-PbO_2" rutile transition was observed five times at 15 kbar and 4 times at 25 and 27 kbar).

At higher pressures rutile goes over into the X phase (Table I); after removal of the pressure the initial "α-PbO_2" structure is restored with an admixture of the rutile modification. These results are well illustrated by Fig. 2 which shows the x-ray patterns of MnF_2 obtained at different pressures.

While the first pattern, obtained at atmospheric pressure, corresponds to the "α-PbO_2" phase with a small admixture of rutile, the second at 27 kbar contains mainly rutile lines and only two or three lines of "α-PbO_2" (in the diagram only one line is shown because the others superimpose on the rutile lines): at 37 kbar (third pattern) an-

TABLE I

MnF_2 (rutile); $p = 1$ bar			MnF_2 (phase X); p=70 kbar		MnF_2 («α-PbO_2») [1]; $p = 1$ bar		
I	*hkl*	*d*, Å	*I*	*d*, Å	*I*	*hkl*	*d*, Å
very strong	110	$3,45_5$	very strong	2.96	strong	110	3.77_1
medium	101	2.73_6	strong	1.84	very strong	111	3.08_5
medium weak	111	2.39	strong	1,81	very weak	002	$2,68_4$
very weak	210	2.18	medium	1,73	weak	021	$2,54_8$
strong	211	$1,82_2$	very weak	1,64	medium weak	102	$2,35_9$
weak	220	1.72_8	medium	1.57	medium	121	2.26_9
very weak	002	1.65_5	medium	1.52	very weak	220	$1,88_2$
very weak	310	1.54_8			very weak	202	1.81_9
weak	301	1.49_1			very weak	130	1.80_{15}
medium weak	112	$1,45_9$			medium	221	1.77_8
					very weak	113	1.61_4
					medium weak	311	1.52_2

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[1] Preliminary patterns indicated that its structure had not changed during the two years which have passed since it was obtained.

TABLE II

Tetragonal ZrO_2 [7]; $a = 5.15$ Å, $c = 5.27$ Å, $z = 4$			MnF₂ (phase X), $p = 70$ kbar; $a = 5.18$ Å, $c = 5.01$ Å, $z = 4$			
I	*hkl*	*d*, Å	*I*	*hkl*	d_{calc} Å	d_{obs}, Å
strong	111	2.99	very strong	111	2.96	2.96
strong	002	2.64				
strong	200	2.57				
strong	102	2.35				
weak	112	2.13				
strong	202	1,84	strong	202	1.80	1.81
strong	220	1.82	strong	220	1.83	1.84
			medium	221	1.72	1.73
			very weak	301	1,63	1.64
medium	113	1.58	medium	113	1.52	1.52
medium	311	1,55	medium	311	1.57	1.57
medium	222	1,50				
weak	312	1.39				
weak	004	1.32				

other two-phase system occurs: rutile + phase X. On the fourth pattern, obtained at 47 kbar, the lines of the X-phase are considerably more intense while the rutile lines are weakened, and finally, after removal of the pressure (fifth pattern) the initial pattern (first pattern) is restored.

The fact that at high pressures $p > 30$ kbar the initial "α-PbO_2" phase (of MnF_2) changes into the rutile phase allows one to conclude that the latter phase is stable in the entire range of pressures up to 30 kbar, and consequently its density at high pressures should be larger or equal to the density of the "α-PbO_2" phase. Unfortunately, our experiment does not allow a sufficiently accurate determination of the x-ray density ρ of both phases at the same pressure; it can only be stated that their densities do not differ by more than two or three units in the second place after the decimal point.

The results allow one to assume that one cannot specify a definite region of equilibrium existence of the "α-PbO_2" phase on the pT diagram. It is very probable that this phase is formed only in the presence of shear stresses which may appear in the camera when the high pressure is removed. The behavior of the "α-PbO_2" phase at high pressures (transition to the rutile modification) favors this point of view, as does the fact that it is precisely these shear stresses which apparently facilitate the transformation of the linear chains of rutile octahedra into the zig-zag shaped chains of the "α-PbO_2" phase.

As has been shown above, an MnF_2 (rutile) → X phase transition takes place at 20-30 kbar where X is the high-pressure phase. The data for the three MnF_2 phases (phase X, rutile, and "α-PbO_2") are presented in Table I. What then is the structure of the high-pressure MnF_2 phase (phase X)?

It turned out that the system of lines of phase X can be indexed in the tetragonal system; the corresponding (hk*l*) indices of the reflections are given in Table II. At 70 kbar the high-pressure phase of MnF_2 has the unit cell parameters: a = 5.18 Å, c = 5.01 Å, Z = 4, and $\rho = 4.59$ g/cm³. The density gain compared with the rutile structure (of MnF_2) is about 18 per cent (if we neglect the effect of the compressibility). The cell dimensions of phase X are close in magnitude to those of the tetragonal modification of ZrO_2,[7] which has a distorted CaF_2-type structure. For comparison, Table II cites data for both phases (the X phase of MnF_2 and the tetragonal ZrO_2), from which it follows that the X-phase lines observed on the x-ray pattern correspond to almost all the strongest reflections of the tetragonal ZrO_2 phase. An exception are only two lines of the X phase—the (221) and (301): they do not appear on the ZrO_2 x-ray patterns and only one of them—the very weak (301)—contradicts the space group D_{4h}^{15}.[7]

There are, thus, grounds for the assumption that at high pressures > 30 kbar there exists a high-pressure phase of MnF_2 which has a distorted CaF_2-type structure; after removal of the pressure it transforms into the "α-PbO_2" phase. It follows from this that the latter cannot be referred to as the high-pressure phase, as was done until now.[1, 2] An analogous situation occurs for CdS,[5] Si,[8] Ge,[9] and apparently InSb;[10] in each case after the removal of the pressure a metastable phase appears as a result of transformation from the stable phase at high pressure.

For this reason, strictly speaking, the concept of high pressure for the metastable modification will be justified only in cases when by direct investigation at high pressures (by x rays, electrical conductivity, etc.) the identity of both structures has been established.

Naturally, it is easier to retain the high-pressure phase under normal conditions if the phase transition at which it is formed occurs at a sufficiently high temperature; a lowering of the temperature and also of the pressure may lead in a number of cases to quenching. Thus, one can hardly doubt that the diamond and rutile modifications of SiO_2 (stepoverite) are high-pressure phases. It is also not surprising that the high-pressure phase of MnF_2, CdS, Si, Ge, and InSb is not retained after removal of pressure, since their phase transitions occur at room temperature.

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