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POLYMORPHISM OF MnF_2 *AT HIGH PRESSURES AND TEMPERATURES*

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The polymorphism of MnF_2 has been investigated by x-ray diffraction techniques at pressures up to 80 kbar and temperatures between 25 and ~400°C. A phase diagram of MnF_2 is presented according to which two phase transformations can be observed at $T > 210°C$ and increasing pressure: one is the rutile → fluorite transformation with a volume discontinuity of ~7 percent and the other is the fluorite → distorted fluorite transformation observed at higher pressures. Only the rutile → distorted fluorite transformation with a volume discontinuity of ~11.4 percent occurs at $T < 210°C$.

FOUR polymorphic modifications of MnF_2 are observed at room temperature and high pressure: for $P < 33 \pm 4$ kbar—MnF_2I, rutile, at 33 kbar $< P <$ 150 kbar—MnF_2II, a distorted fluorite phase,[1] and at $P > 150$ kbar—MnF_2III, an orthorhombic modification of the $PbCl_2$ type.[2] After lowering the pressure a metastable MnF_2IV phase, isostructural with α-PbO_2 was observed under normal conditions.[1,3,4]

In this work we have investigated the polymorphism of MnF_2 by x-ray diffraction methods at high pressures up to 80 kbar in the temperature range from room temperature up to ~400°C. For this purpose we used an x-ray camera which makes it possible to obtain Debye-Scherrer patterns of substances which are simultaneously under high pressure and at high temperature.[5] In carrying out the experiments we added to the investigated MnF_2 samples NaCl which served as an internal pressure manometer. The pressure was estimated by means of Decker's semi-empirical equation of state for NaCl.[6] The latter makes it possible to estimate the pressure at temperatures up to 1500°C from the change of the lattice parameter of NaCl $\Delta a/a_0 = (a_P - a_0)/a_0$ where a_0 and a_P are the values of the parameter under normal conditions (P = 1 bar and T = 25°C) and under high pressure and high temperature conditions.[1)]

The use of NaCl made it possible to measure the pressure in each specific experiment up to ~40 kbar with an accuracy of ±2 kbar and for $P > 40$ kbar with an accuracy of ±3 kbar. The error in the temperature determination did not exceed ±5°C.

The obtained results showed that in addition to the previously known MnF_2I, MnF_2II, MsF_2III, and MnF_2IV modifications, a cubic MnF_2V phase with the fluorite structure exists in the investigated pressure and temperature range. Table I shows the x-ray data for the MnF_2V phase at T = 400°C and P = 40 kbar. The average value of a obtained from these data is $a = 5.192 \pm 0.006$ Å. It has been established that after the cubic phase appears at high pressure and high temperature it continues to exist at room temperature and high pressure. On this basis one can assume that it may be possible to retain the MnF_2V phase at atmospheric pressure and low temperature.

Table I

I^*	hkl	d_{meas}, Å	d_{calc}, Å	I^*	hkl	d_{meas}, Å	d_{calc}, Å
s	111	2.996	2.997	vw	222	1.502	1.493
w	200	2.600	2.596	vw	400	1.299	1.293
m	220	1.833	1.835	w	331	1.189	1.191
m	311	1.567	1.565	w	420	1.160	1.161

*The intensity of the line I is denoted by: s—strong, w—weak, m—medium, and vw—very weak.

A detailed x-ray investigation in a broad temperature range made it possible not only to prove the existence of a fluorite MnF_2V phase, as was the case with ZnF_2,[5] but also to determine its location on the phase diagram. Figure 1 shows the phase diagram of MnF_2 set up on the basis of the results of this work. The experiment was carried out in the following order: a series of x-ray patterns was obtained at constant temperature and gradually increasing pressure. In a number of experiments the x-ray patterns were also obtained on lowering the pressure. According to the data obtained, two polymorphic transitions are observed on increasing the pressure from 1 to 80 kbar in the 420-250°C temperature range: the first MnF_2I → MnF_2V (rutile → fluorite), and the second MnF_2V → MnF_2II (fluorite → distorted fluorite). X-ray patterns in the same pressure range and at temperatures of 25-200°C established one phase transition MnF_2I → MnF_2II (rutile → distorted fluorite).

The equilibrium boundaries between phases I and V (AB), as well as between V and II (CB) were drawn on the basis of data at 420 and 315°C. The line of transformation of phase I → II (BD) joins the point of this transition at T = 25°C and $P = 33 \pm 4$ kbar with the point of intersection of the phase boundaries AB and CB. The accuracy in the placement of the phase boundaries AB, CB, and BD is shown in Fig. 1 by means of arrows.

The P-T diagram of MnF_2 thus obtained should have a triple point with the coordinates $P \approx 33$ kbar and $T \approx 210°C$. However, we did not succeed in this work in observing the triple point directly from the x-ray patterns; this can be explained by the following reasons: 1) the presence of a considerable kinetic lag of the polymorphic transformations in MnF_2 which are very noticeable for $T < 300°C$; 2) the difficulty in the interpretation

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[1)] We take the opportunity to express our sincere gratitude to Professor T. Hall for sending us tables for estimating the pressure in accordance with Decker's data.

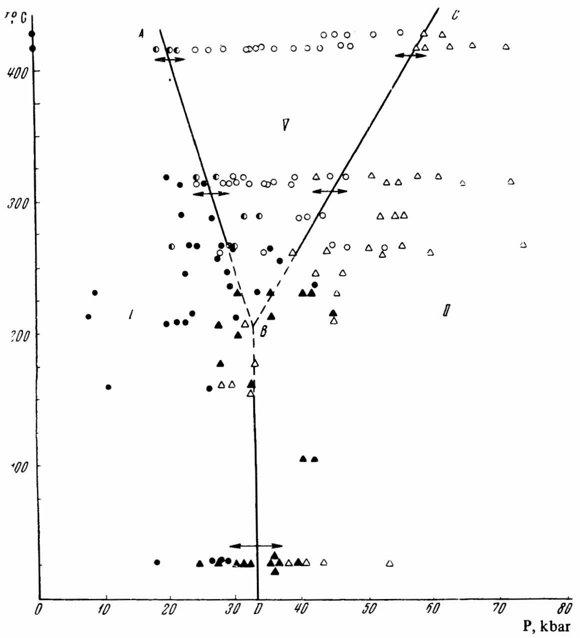

FIG. 1. Phase diagram of MnF_2. Notation: ●–MnF_2I, ○–MnF_2V, △–MnF_2II, ◐–mixture of phases I and V, and ▲–mixture of phases I and II.

of x-ray patterns resulting from the superposition of the diffraction patterns of MnF_2II and MnF_2V which are very similar to one another. The latter circumstance makes it difficult not only to locate the triple point but also to determine the boundary CB.

The distortion of the cubic structure in the V → II phase transition manifests itself in the fact that along with the deformation of the unit cell (212) and (013) superstructure reflections appear on the x-ray patterns; the (311) line becomes gradually weaker and diffuse and splits, as a result of which a (113) and (311) doublet is formed. One cannot at present answer unambiguously the question whether the process of distortion of the cube is continuous or sudden. It is difficult to determine where the cubic structure ends and the distorted structure begins. In this work we have stipulated that the structure is distorted from the time when the (311) line is split.

Regardless of all the difficulties of the investigation, the aggregate of the obtained data allows one to conclude that the triple point lies on the straight line DB in the temperature range 160–210° C.

Observations of the I → V polymorphic transition allow one to assume that an intermediate phase exists on the rutile-fluorite boundary. Indeed, a consideration of the two-phase x-ray patterns at temperatures of 300–400° C and pressures of 15–25 kbar indicates that it is possible under these conditions to superimpose on the diffraction pattern of MnF_2I the diffraction from orthorhombically distorted fluorite; on further increasing the pressure the photographs indicate the pure cubic MnF_2V phase. Such an assumption is based on the following facts: 1) the error in the determination of the unit-cell parameter of fluorite at low pressures is comparatively large—about ± 0.02 Å, whereas at higher pressures it amounts to ± 0.002–0.004 Å: 2) the x-ray patterns of pure fluorite often include the (210) superstructure line which increases in a number of instances the error in the determination of a_{cub} to ± 0.01 Å; 3) in one of the experiments at T = 400° C and low P an x-ray pattern was obtained which corresponds to the α-PbO_2 phase. It is, therefore, quite possible that if it exists, the proposed intermediate modification is indeed the α-PbO_2 phase (MnF_2IV).

If one continues the line AB in Fig. 1, it will intersect the temperature axis at $T \approx 740°$ C. Taking into account the fact that the melting point of MnF_2 is 856° C, one can assume that at atmospheric pressure and high temperature before melting there exists a fluorite phase MnF_2V. This assumption was checked at our request by V. M. Agoshkov by means of differential thermal analysis of MnF_2. He observed at a temperature of 710 ± 5° C and P = 1 bar a polymorphic transition with evolution of heat which apparently corresponds to the rutile-fluorite (MnF_2I → MnF_2V) transition.

As has already been noted above, the investigation of the phase diagram of MnF_2 is complicated by hysteresis phenomena. Hysteresis is characteristic of first-order phase transitions. It has been shown in [7] that even the comparatively rapid BiI → BiII transition is accompanied by considerable hysteresis: for a cylindrical sample ~ 0.024 mm in diameter enclosed in NaCl it amounts to 5.3 kbar and for a platelet ~ 0.005 mm thick it is 2.8 kbar. The authors of [7] consider the principal reasons for such a hysteresis to be the complex growth process of nuclei of the new phase surrounded by the crystalline bulk of the initial modification as well as the pressure gradient appearing in the investigated sample and in the pressure transmitting medium as a result of the volume jump accompanying the phase transformation. The tendency of MnF_2 to form metastable phases (IV–α-PbO_2, P = 1 bar and T = 25° C; V–fluorite, T = 25° C, P = 20–30 kbar) is an extreme manifestation of hysteresis.

In order to study the hysteresis in the V ⇄ II transition, we took a series of x-ray patterns successively crossing the boundary CB in one and then in the opposite direction, i.e. with increasing and decreasing pressure. It turned out that whereas in going in one direction one observes phase II at 400 or 300° C and P = 60–70 kbar, a decrease of the pressure by ~ 30 kbar does not lead to a complete re-establishment of the cubic structure, although the distortion of the cube undoubtedly decreases. It follows hence that on the boundary BC at these temperatures the hysteresis exceeds 30 kbar and therefore if one succeeds in obtaining the cubic MnF_2V phase on decreasing the pressure, then this will only occur for $P < 30$ kbar.

We carried out no special investigation of the hysteresis of the phase transitions on the boundaries AB and DB. However the presence of considerable volume discontinuities in the polymorphic transformations of phases I → V and I → II made it possible to observe in many experiments a considerable pressure drop during the formation of new phases; this is one of the principal causes of hysteresis. The sluggish nature of these phase transitions which increases with decreasing temperature and leads to appreciable kinetic lags (Fig. 1) is undoubtedly a result of the hysteresis.

We obtained, along with the phase diagram, data on the pressure variation of the parameters and volume of the unit cell of the various modifications of MnF_2 at

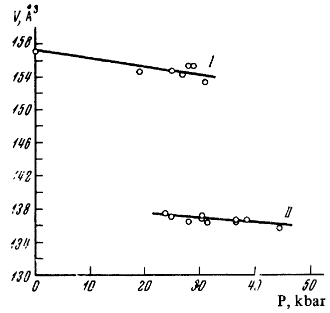

FIG. 2. The variation of the unit-cell volume of MnF_2I and MnF_2II with pressure at 25°C.

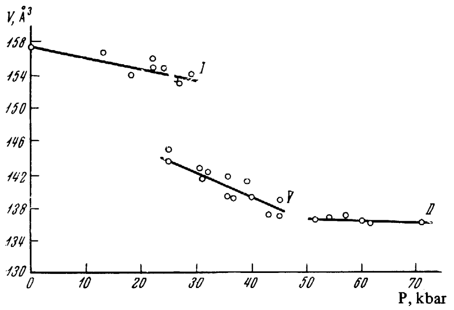

FIG. 3. The variation of the unit-cell volume of the phases MnF_2I, MnF_2V, and MnF_2II with pressure at 315°C.

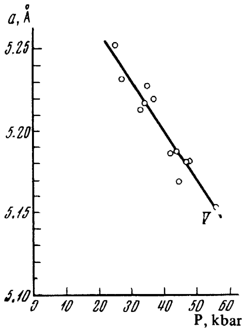

FIG. 4. Variation of the unit-cell parameter of MnF_2V with pressure at 420°C.

various temperatures. Figure 2 shows the V(P) dependence for MnF_2I and MnF_2II for T = 25° C up to pressures ~50 kbar on which one can clearly see the volume jump $\Delta V/V \approx 11.4$ percent (25–30 kbar) at the I→II phase transition. Figure 3 shows the volume variation of MnF_2 at T = 315° C and pressures up to ~75 kbar; two polymorphic transitions take place under these conditions: I→V with a volume discontinuity ~7 percent (25–30 kbar) and the V→II transition.[2)] It is seen from the figure that the experimental accuracy does not allow one to answer the question whether there is a volume discontinuity at the second phase transition. It is also obvious (Fig. 3) that the compressibility of MnF_2V exceeds appreciably in its magnitude the compressibility of phases I and II. Thus there is in the case of MnF_2 an "anomaly"—the high-pressure phase (V) has a larger compressibility than the low-pressure phase (I). It is very likely that it is precisely this "anomaly" which is the reason for the phase transition MnF_2V → MnF_2II and thus determines the relatively narrow region of the stable existence of the fluorite modification (MnF_2V) on the P-T diagram.

The obtained data (Fig. 4) make it possible to estimate the interatomic distances Mn-F and F-F in the MnF_2V structure which are directly expressed in terms of the unit-cell parameter a in the form $a\sqrt{3}/4$ and a/2. As follows from the results of the calculation (see Table II), the Mn-F distance is close to the sum of the ionic radii of fluorine and manganese (2.24 Å) and changes little with pressure and temperature. Thus, unlike in the phases I[8] and IV,[3] in the V modification the bonding is purely ionic.

It can be assumed that the P-T diagram shown in Fig. 1 is characteristic of many fluorides and oxides with the initial rutile structure. Such a conclusion follows from the analogy of their behavior at high pressures. In fact, as was previously shown,[2] CoF_2, NiF_2, as well as MnF_2, undergo at high pressures and room temperature a polymorphic transition from rutile to the distorted fluorite type. The fluorite phase observed in MnF_2 at high pressures and temperatures above 250° C was observed in ZnF_2[5] for T = 300° C and P = 80 kbar; it was also possible to obtain it in PbO_2.[9] Finally, the metastable α-PbO_2 phase has been established for MnF_2,[1,3,4] ZnF_2,[4] PbO_2,[10] and TiO_2.[11]

Taking into account the data known at present, one can assume that the boundaries of the regions of existence of fluorite on the phase diagrams in the case of MnF_2 and PbO_2 are shifted towards lower pressures compared with CoF_2, NiF_2, ZnF_2, and TiO_2. Thus, the polymorphic rutile–fluorite transition at high pressures and temperatures can apparently be expected for a whole series of compounds with the rutile structure.

Table II

Phase	P, bar	Mn–F distance, Å		F–F distance, Å	
		25° C	420° C	25° C	420° C
MnF_2 V	$20 \cdot 10^3$	2.263	2.277	2.613	2.629
	$35 \cdot 10^3$	2.240	2.258	2.587	2.607
	$50 \cdot 10^3$	—	2.238	—	2.585
MnF_2I [8]	1	2.10—2.13	—	—	—
MnF_2 IV [4]	1	2.07—2.17	—	—	—

Let us try to present the geometrical process of the rearrangement of the rutile structure (MnF_2I) into the fluorite structure (MnF_2V). According to the results of this work for P ≈ 25 kbar and T = 300° C the unit-cell parameters of the rutile modification are a = 4.815 Å and c = 3.310 Å; the unit-cell parameter of fluorite a = 5.236 Å.

Figure 5 shows a diagram of two unit cells of the fluorite structure. We choose in the fluorite structure a tetragonal cell with the axes $a_{tetr} = a_{cub}/\sqrt{2} = 3.703$ Å and $c_{tetr} = a_{cub} = 5.236$ Å (Fig. 5a). The coordinates of the atoms in the "new" unit cell will be:

$$2Mn - 000,\ {}^1/_2{}^1/_2{}^1/_2;\ 4F - 0{}^1/_2{}^1/_4,\ {}^1/_20{}^1/_4,\ 0{}^1/_2{}^3/_4,\ {}^1/_20{}^3/_4.$$

In the rutile structure (Fig. 5b) the atoms occupy the following positions of the space group D_{4h}^{14} (P4/mnm):[12]

$$2Mn - 2(a)\ 000,\ {}^1/_2{}^1/_2{}^1/_2;$$
$$4F - 4(f)xx0,\ \bar{x}\bar{x}0,\ ({}^1/_2 - x)({}^1/_2 + x){}^1/_2,\ ({}^1/_2 + x)({}^1/_2 - x){}^1/_2.$$

It is known that in the space group D_{4h}^{14} there is a 4(d)

[2)] The strongest reflections, (111), (200), (220), and (311), were used in calculating the parameter and volume of the unit cell of phase V (Figs. 3 and 4).

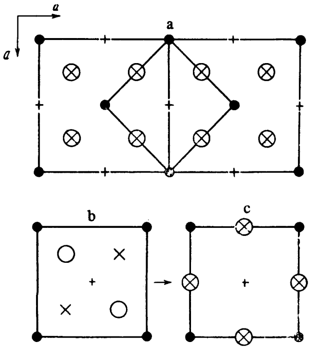

FIG. 5. Schematic diagram of the rearrangement of the rutile structure into the fluorite structure: ○ and ×—fluorine atoms at a height of 0 and ½ respectively, ● and +—manganese atoms at a height of 0 and ½; a circle with a cross corresponds to two fluorine atoms one above the other at a height of ¼ and ¾ respectively from the plane of the projection. a—projection of the positions of the atoms in the fluorite structure on the (001) plane: choice of the tetragonal unit cell with the parameters $a_{\mathrm{tetr}} = a_{\mathrm{cub}}/\sqrt{2}$, and $c_{\mathrm{tetr}} = a_{\mathrm{cub}}$. b—positions of the atoms in the rutile unit cell. c—hypothetical structure: the fluorine atoms in the rutile structure occupy the 4(d) position and the manganese atoms occupy the 2(a) position.

position with the coordinates 0 ½ ¼, ½ 0 ¼; 0 ½ ¾, ½ 0 ¾. Therefore, if it were possible to shift in the rutile unit cell the fluorine atoms from the 4(f) position to the 4(d) position, without at the same time shifting the manganese ions, then the positions of the atoms would correspond to the fluorite structure (Fig. 5c). However, such a rearrangement is impossible without deformation of the unit cell. In fact, the fluorine atoms occupy in the fluorite the corners of a cube whose edge is a/2 = 2.618 Å. If they are shifted in the rutile unit cell from the initial 4(f) position into the 4(d) position, then they will occupy the corners of a right-angle parallelepiped whose sides are 3.405 × 3.405 × 1.655 Å. Thus the displacement of the fluorine ions in the phase transition rutile → fluorite under high pressure should be accompanied by deformation of the unit cell: simultaneously with being hydrostatically compressed, it must be expanded along c.

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